PRACTICAL CHEMISTRY
FOR MEDICAL STUDENTS

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BY

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EDINBURGH
E. & S. LIVINGSTONE LTD.
16-17 TEVIOT PLACE
1946

FOREWORD

Chemistry is essentially an experimental science, and as such it cannot be properly studied unless the student carries out with understanding a properly arranged series of laboratory experiments related to, and illustrative of, the facts which are presented to him in the lecture theatre. This is a statement with which few teachers of chemistry would disagree, but it is unfortunately true that in some universities little more than lip-service is paid to the importance of laboratory work. Only too often courses in practical chemistry are of the " cookery book " variety, in which the student is left to follow blindly, and without any proper understanding of the theoretical basis of what he is doing, the " recipes " given to him.

In 1939 I asked my colleague, Mr. Klyne, to reorganise entirely the course in practical chemistry given to medical students in the University of Edinburgh in such a way as to emphasise the close relationship between the theoretical and practical courses, and so as to provide a better training in the laboratory techniques likely to be useful to the medical student in his subsequent career. This reorganisation has been carried out over a number of years and has been the subject of much interesting experimentation in teaching methods. While neither Mr. Klyne nor myself would venture to claim that his present course is an ideal one, we do believe that in certain respects it may be more suited to the particular needs of the medical student than some of the courses given elsewhere, and we both feel that a most satisfactory degree of correlation between the lecture and laboratory courses has been attained.

Mr. Klyne's book is based on the courses in practical chemistry given to " pre-medical " and first-year medical students in this University at the present time, and in it he has incorporated most of the ideas concerning the teaching of practical chemistry which he has developed during recent years. I should perhaps emphasise that at present the time allotted to chemistry in the medical curriculum at Edinburgh does not permit us to cover more than about half of the work in this book. We believe, however, that in an ideally-arranged medical curriculum in which due importance is attached to the fundamental sciences, a course covering most of the ground dealt with in this book represents the minimum of instruction in practical chemistry which the medical student should receive.

Perhaps one of the most important functions of a chemistry course in the medical curriculum is that it provides an early opportunity of training the medical student in general scientific principles and methods —an opportunity that only too often is missed. Part One of this book, in which such matters are discussed, could be read, I believe, with

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great benefit not only by medical students, but also by first- and second-year university science students.

I hope that the publication of this book may fill a long-felt want in this and other university medical schools, and it gives me much personal pleasure to congratulate Mr. Klyne most warmly in his achievement, which represents, I believe, a substantial contribution to medical education. ·

G. F. MARRIAN.

PREFACE

Any elementary course in science has four purposes, namely :

(1) Instruction in scientific method.
(2) Instruction in the principles of the science under consideration (*e.g.*, physics, chemistry or biology).
(3) Instruction in the experimental methods of the science under consideration.
(4) Presentation of a selection of the facts of the science. These include (*a*) facts necessary to illustrate the principles of the subject, (*b*) facts likely to be of direct value to the student in later work (*e.g.*, in medicine, industry or agriculture).

If a course is to be truly scientific, it must do more than merely offer to the student a series of facts ; it must be presented in such a way that emphasis is laid on the methods of thought by which the facts have been discovered and related to one another, and by which all further experiment will be guided. The work done by the student himself, *i.e.*, the practical part of the course, offers the best opportunity for encouraging him to think scientifically. The physical sciences (physics and chemistry) studied during the early part of the medical curriculum provide a necessary foundation of fact for the study of life as a physicochemical phenomenon in subsequent years. They also offer a training-ground, excellent because of the simplicity of the material involved, for the practice of scientific method.

In this book, the result of ten years' experience in teaching in the University of Edinburgh, I have tried, so far as practical chemistry is concerned, to serve all the four purposes listed above. Training in scientific method has been emphasised in two ways. First, three chapters on scientific method have been included, which will, I hope, be treated not as a separate part of the work to be mastered for examination purposes, but as an outline of the ideas underlying every experiment done. Frequent reference to these chapters will be necessary if the student is to get the most out of his laboratory work. Secondly, each part of the work has been presented as systematically as possible to emphasise not only chemical principles but also general principles of scientific method. This systematic treatment is in part responsible for the large bulk of the book, especially in the chapters on descriptive inorganic and organic chemistry.

The scope of this book is governed largely by the present medical curriculum in the University of Edinburgh. Here, general and in-organic chemistry, together with a little physical chemistry, must be studied (in a Pre-Registration Course at the University, or its equivalent

at school) before the student is admitted to the Faculty of Medicine. Physical and organic chemistry are studied during the first year of the medical curriculum, and biochemistry is studied in the Physiology Department during the second year.

This book covers the practical work which should be done in the Pre-Registration and First Year Courses. It does not include preliminary work which should have been done in General Science in the early years of a secondary school course (e.g., experiments on physical and chemical changes, on the laws of proportion, or on mixtures and compounds). The book does *not* cover biochemistry proper, although reactions of some biologically-important compounds are included.

It is hoped that the book will be useful for medical chemistry courses elsewhere and for similar courses of intermediate standard, e.g., veterinary, dental and dietetics courses.

The book contains far more experiments than can be included in any medical chemistry course to-day—and indeed more than could be included in an ideal course of the future. Instructors will therefore need to choose a selection of experiments from each branch of the work.

The book is divided into five parts as follows :

I. Some Fundamental Scientific Ideas.

This part deals briefly with some ideas that form the basis of work in all branches of science. It may seem to some readers too highflown for a first-year course, and to others too obvious to need inclusion. To both sets of readers I must point out that they will use these ideas continually in all their later work, because these ideas are not merely chemical, but common to all organised thinking. I am very glad that several medically-qualified colleagues, whose business it is to teach the student in his later years, have heartily approved the inclusion of this part.

II. Practical Methods.

This part describes the handling of apparatus and materials in the laboratory ; it should be supplemented by practical demonstrations. It is most important that the student should make a habit of clean and orderly practical work as soon as possible. Furthermore, many of the practical methods described here will be used again in later work.

III. General and Physical Chemistry.

This part deals with some general physico-chemical principles which are of value in understanding biological phenomena. The most important general idea which the student has to grasp here is that of dynamic equilibrium.

It is impossible to include experiments on the fundamental laws of chemistry, except in so far as volumetric analysis illustrates the Law of Constant Proportions. The reasons for this omission are (1) lack of space, (2) the fact that lack of time and apparatus prevents

us from introducing these experiments into our own Pre-Registration Practical Course, (3) the fact that such experiments are well described in many elementary practical books.

Chapter 6 treats briefly some theoretical principles, chiefly the Law of Mass Action and the Ionic Theory, and their applications.

Chapter 7 deals with volumetric analysis, which is important because it is a method widely used in all branches of chemistry, and because it is the only quantitative work which can be introduced into most medical chemistry courses.

Chapter 8 gives details of a few simple experiments in physical chemistry. Lack of time and apparatus limits what can be done in the laboratory.

IV. Inorganic Chemistry.

This Part covers the descriptive inorganic chemistry which it is possible to illustrate in an elementary practical course, and the application of this to the identification of simple substances.

V. Organic Chemistry.

This Part covers the chemistry of simple representative compounds of carbon (the " grammar " of organic chemistry) and the application of this to some compounds of biological importance. The relation between the different chapters of this Part are explained in Chapter 11.

The student should at all times try to relate his theoretical and practical work to one another. This is easy to say, but difficult to do. It is, however, well worth the effort, since without some connection between theoretical and practical work formulae are patterns on paper without any meaning in fact, and laboratory tests are a collection of cookery recipes. I hope that the theoretical explanations in this book will help to link theory and practice together, although they cannot take the place of a theoretical text-book.

The subjects most obviously related to chemistry are biochemistry and physiology. Many references to the connections between chemistry and these subjects are given in this book, since a medical chemistry course is of little value unless the student realises how intimate is the relationship between these subjects. I am indebted to the staff of the Physiology Department in this University for permission to adopt some of their experiments, so as to link the two courses more closely together.

The applications of chemical methods to clinical medicine and pharmacology are also mentioned where relevant. It is hoped that these references will help the student to use chemical methods in these subjects intelligently when occasion arises.

It is sometimes difficult to convince the student of the need for taking trouble over experiments where someone else knows the answer before he starts. This is particularly true as regards the keeping of records. The student must realise that, while in his university course

he has a demonstrator or text-book to tell him the answer at every turn, this will not be the case when he comes to medical practice or to research. He will then have to depend on his own observations. Unless he has learnt to observe, to make deductions and to write reports during his student days, he will probably make many serious mistakes in practice.

The student is often confused about the difference between *knowing something* and *knowing where to look it up*. In any science he must know the principles and understand how to apply them to individual facts, he must know a representative selection of facts to illustrate the principles and he must know those facts which he is going to use in practising or applying his subject. So far as the remaining facts of the subject are concerned, the student should *not* learn them, but should know where to find them when he wants them. Every instructor will have his own ideas as to the facts which the student should remember, and he should make sure that the student is acquainted with his views. This book contains many facts—for example, all the less important reactions of the inorganic ions—which anyone who is not specialising in chemistry should *not* be expected to remember. They are included for reference when required.

Books in which further information may be found are listed at the end of each chapter. These books are of several kinds, viz., theoretical text-books, other elementary practical books dealing with subjects not covered here, and advanced books for use if the reader wishes to study any part of the subject in detail.

The student must realise that every elementary text-book contains many broad general statements to which there are exceptions, sometimes numerous. If the subject is studied more fully, these exceptions become important, and the student is apt to be critical of the general statements. These generalisations are, however, essential in trying to give a bird's-eye view of a whole subject, since without them the reader is confused by a mass of detail.

In nearly every branch of science different systems of nomenclature exist side by side in spite of all attempts at standardisation. In an elementary book it is impossible to discuss all the common systems of nomenclature; one system only is used in this book, although there may be other systems equally good, which the student will probably encounter in other places.

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Many friends, some of whom are named below, have helped in the production of this book. I am very grateful to all of them, for without their combined help this book would not have been written. I must make it clear, however, that I am responsible for any errors or short-comings which may be found in the work.

I must first thank *Professor Marrian for having given me the opportunity* since 1939 of reorganising the practical courses in medical chemistry in this Department, for writing the Foreword, and for help at all stages in the growth of this book.

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PART ONE

SOME FUNDAMENTAL SCIENTIFIC IDEAS

CHAPTER I

THE NATURE OF SCIENTIFIC WORK

I, I   SCIENTIFIC METHOD AS ORGANISED COMMON-SENSE

Many students consider scientific method as something apart from everyday life, yet anyone who thinks in an organised common-sense way uses the scientific method. A motorist who tries to find out why his car will not go should apply the scientific method as much as a chemist making an analysis or a medical man making a diagnosis. All are, or should be, examining the facts of the particular problem before them, and applying to the problem the knowledge of the subject which they and others have previously gained by experience.

This way of thinking, which we call the scientific method, turns on one fundamental assumption, *i.e.*, that the *same cause* will always produce the *same effects*.

The student must realise that the methods of reasoning which he ̣ ̣ ̣ ̣ ̣ ̣ ̣ ̣ ̣ ̣ ̣ ̣ ̣ ̣ ̣ ̣ ̣ ̣ ime as t he is ̣ ̣ ̣ Chem- ̣stry course will be equally if not more important in the handling of quantitative data in clinical work.

The word " science " is used with at least two different meanings. It is used sometimes to denote the whole body of known facts about the natural world, and sometimes to denote the organised common-sense way of thinking discussed above. It is better to use the term " science " for the body of facts, and the term " scientific method " for the way of thinking.

Careful observation is the basis of all scientific work. Sometimes the worker observes the facts supplied by nature without interfering himself, and discovers the relations between them if possible. In other cases he does interfere in the natural course of events ; he " puts the question to nature " by an *experiment*, observes the results, and if possible discovers the relations between them and other known facts.

I, 2   CAUSE AND EFFECT

It has been stated above that all scientific work is based on the idea that the same cause always produces the same effect. Conditions in

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which there is only one cause and one effect are rare. A very large part of all scientific work consists in disentangling effects from one another and causes from one another, and in trying to link one effect with one cause. This is especially true of medicine.

A common method of experiment is to vary each possible cause separately. If in any process possible cause A is varied and there is no change in any effect, then A is not a cause of any effect and may be disregarded. If variation in possible cause B causes change only in effect Z, then Z is the effect of B and B is the cause of Z.

The following simple example shows how a problem which often arises in the laboratory may be solved by varying the circumstances. Suppose a student is carrying out the reactions of the nitrate ion, using a solution of barium nitrate. He finds that, contrary to what his text-book tells him, a precipitate is formed when he adds silver nitrate solution to his barium nitrate solution. Some possible causes for the unexpected result are :

1. Dirt in the test-tube used for the reaction (anything which gives an insoluble silver salt, e.g., chloride).

2. Impurity in the barium nitrate solution (e.g., chloride).

3. Impurity in the silver nitrate solution (anything which gives an insoluble barium salt, e.g., sulphate).

Experiments to decide which possible cause is the true cause of the unexpected result might be carried out as follows :

Cause varied	Experiment	Result	Conclusion
1	Repeat test with a tube known to be clean	No precipitate.	Original tube was dirty. (1) is true cause.
		or Precipitate formed.	Original tube was not dirty. (1) is not true cause.
2	Repeat test with barium nitrate solution known to be pure.	No precipitate.	Original barium nitrate solution contained impurity. (2) is true cause.
		or Precipitate formed.	Original barium nitrate solution contained no interfering impurity. (2) is not true cause.
3	etc.	etc.	etc.

More detailed rules for relating effects and causes are given in text-books on scientific method (e.g., Westaway, Scientific Method, 4th edition, 1931, chap. 17).

I, 3

EVIDENCE

Evidence in scientific work may be of two kinds. It may be the result of the worker's own observations, or the result of other people's observations. In both cases the worker must always be ready to suspect that the evidence is wrong, and to check it if possible.

The worker's own observations are the easiest to check. If the experimental material is still available, he can in case of suspicion repeat the observations himself, or have them repeated by someone else in whom he has confidence.

Other people's observations vary greatly. They may be the observations of an experienced scientist using apparatus of proved accuracy, reported in an honest and intelligible way. Even in this almost ideal case there is room for suspicion, and the work must be repeated by someone else with new apparatus if necessary. At the other end of the scale is the case-history of a child who cannot talk, taken from an unintelligent mother by an inexperienced student. Here everything will need to be verified if possible. The student will meet examples of every kind between these two extremes. The watchword must always be " Suspect and check."

The importance of *negative* evidence needs to be stressed. The fact that a particular precipitate is *not* formed in analysis or that a particular sign is *not* found during the examination of a patient is just as important as the formation of a precipitate or the finding of a sign. Whenever written records are kept, negative evidence must be noted as carefully as positive evidence. The temptation to note down only the parts of the evidence where something positive is seen must be resisted. In medicine, negative evidence often plays the major part in reaching a diagnosis or determining treatment. The extent to which evidence which apparently leads to a definite conclusion needs confirmation depends on the purpose of the work in hand.

I, 4

TYPES OF SCIENTIFIC WORK

There are two main types of scientific work. The first is the application of general principles to explain particular cases (*e.g.*, to determine the nature of a compound, or to diagnose a patient's illness). This is called *deduction* and most routine scientific work (including medical work) falls into this class.

The second type of work is the formulation of general principles to link together a whole series of facts (*e.g.*, the formulation of a theory to account for the abnormal osmotic pressures and the conductivities of electrolytes). This is called *induction*, and all fundamental research belong to this class. Each stage in research of this kind usually goes through the following steps :

1. The investigator is impressed by a series of apparently isolated observations.

2. He forms a mental picture (hypothesis) which he thinks will link them together.

3. He tests his mental picture by carrying out experiments to see whether it predicts the results correctly. At this stage the investigator must be relentlessly self-critical. He must, in fact, do his utmost to disprove his own ideas.

4. If the results of the experiments support his mental picture, he is satisfied that this is in some way a representation of the truth. If the results show that the hypothesis is a correct statement of fact summarising many individual phenomena, it is called a *law* (*e.g.*, the Law of Constant Proportions). If the hypothesis involves suppositions which cannot be proved or disproved as statements of fact, but which are well supported by indirect experimental evidence, it is called a *theory* (*e.g.*, the Atomic Theory).

5. If the results do *not* support the mental picture, the latter is *scrapped* and a new one made and tested.

Similar steps are then followed for the next stage of the research; throughout the work, thought and experiment alternate with one another.

1, 5   THE DESIGN OF EXPERIMENTS

The following rules will serve as a guide in the design of experiments:

1. *Object.*
This must be clear, otherwise no results of value will be obtained. The object in original work is usually to test the truth of a hypothesis based on previous experience.

2. *Previous Work.*
Before the experiments are planned, all the relevant information available should be studied; it should not, however, be allowed to bias the worker's views unduly.

3. *Nature of Experiments.*
If the object is clear, and previous knowledge regarding it has been digested, it should be easy to decide the *nature* of the experiments necessary to fulfil the object, although it may be difficult and often impossible to do the necessary experiments. Where a cause-and-effect relationship is being studied, the ideal method of experiment is to vary each possible cause separately while controlling (*i.e.*, keeping constant) all other possible causes. Controls are considered further on pp. 12, 17 and 19-20.

4. *Number of Experiments.*
A sufficient *number* of experiments must be done. Statistical method will indicate the minimum number necessary to give results of real value.

5. *Materials and Methods.*

These must be adequate for the work in hand, otherwise the experiments might as well not be done. It would be wrong to say simply that apparatus must be clean, reagents pure, and methods accurate, since absolute cleanliness, purity and accuracy are unknown. It is correct to say that the imperfections of materials and methods must be such that their influence on results can be neglected or allowed for. It is a waste of time to make one stage of a process much more accurate than another (*e.g.*, to weigh a substance on a balance with an accuracy of 1 in 10,000 and then titrate it, using a burette the accuracy of which is 1 in 200).

6. *Reports.*

These must be complete and honest (see the following section).

1, 6   THE KEEPING OF RECORDS

An essential part of any scientific work is the writing of a report of what the worker has done and seen—a description which will enable him, or anyone else with a knowledge of the subject, to repeat it without further guide.

The report must be an *honest* description of everything that has been done and seen. An account which leaves out awkward facts that do not fit in with first impressions, or an account which describes what the book says should have happened instead of what *did* happen, is useless. It may satisfy a desire for quick results, but omissions and false statements will certainly be found out if anyone else repeats the work. Every medical practitioner's results are liable to be examined at some time and he must be in a position to justify them. Any details that might possibly be of significance should be reported, since data which do not immediately seem important may be of value in the light of future work. Mistakes should be crossed out lightly, so that the original statements are legible, and pages should *not* be torn out of note-books.

The report should be as brief as possible, provided that it is clear. Where a method given in a text-book or journal is being followed, it is sufficient to refer to this provided that (1) the reference is complete and clear, (2) any alterations in the conditions of experiment are noted specially, (3) any occurrence not in accordance with what the book says is noted specially. Notes should be made in a fixed-leaf note-book [1] —*not* on odd scraps of paper which may be lost—and they should be written in ink. The *original* notes must be kept: a "fair copy" is open to the objection that mistakes may have been made in copying. Notes must be made immediately after each stage of the work; it is fatal to trust to memory longer than is necessary.

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[1] This applies to consecutive work. Where data are collected at intervals over a long period, *e.g.*, case histories, loose record cards in a filing cabinet are preferable.

It is particularly important that numerical readings should be noted immediately and checked by re-observation before anything else is done. The few seconds taken at each stage by this checking may, by correcting an error in reading, save the hours or days necessary for the repetition of an experiment. *Units* must always be stated and the actual readings must be noted. If this is done, the calculations depending upon them can be checked subsequently, and if a mistake in calculation has been made, it will be corrected. If, however, the note-book contains not the actual readings, but only figures derived from them—by addition or subtraction, carried out mentally or on " rough paper "—the arithmetic cannot be checked.

The note-book should be kept as neat and orderly as possible, not because neatness is an end in itself, but because it makes the notes easier for anyone to read, and contributes to the accuracy and completeness of the work.

In many cases results can be understood more easily if presented graphically. It must, however, be realised that graphs can easily deceive, and in all cases the data from which they were plotted must be kept. The choice of scales in the graphical presentation of results is important.

The *final result* of any part of the work—*e.g.*, the concentration of a solution deduced from a titration result—must be *stated clearly* and *boldly* so that the result and its meaning can be picked out at a glance. At the end of any large piece of original work, a short account such as would form a paper in a scientific journal should be written, so that the worker can quickly refer to the object, method and results of the work. In all cases, however, the original laboratory notes *must* be kept.

1, 7   DIFFERENCES BETWEEN THE PHYSICAL AND BIOLOGICAL SCIENCES

Although scientific method is common to all branches of natural knowledge, the application of the method in the biological sciences differs in some important respects from its application in the physical sciences, on account of differences in the experimental material.

The physical scientist rarely studies individual units of matter and energy such as molecules, atoms, electrons or quanta. As a rule he studies samples consisting of very large groups of units, and deduces the properties of an average unit from the behaviour of these samples. Since the samples are so large, the averages for two or three samples of material are likely to give a close approximation to the true average. It is relatively easy to obtain homogeneous materials, and therefore sampling is easy. Further, it is possible to prepare two or more objects (*e.g.*, 1 gram weights) which are identical within the limits of experimental error.

The biological scientist, however, usually works with relatively small numbers of units (*e.g.*, men or dogs), measuring the properties of individual units, and trying to deduce from these the properties

of an average unit. The variations between units are so large that the properties of an average unit cannot be defined with the precision possible in physical science, and statistical methods must always be used to determine the real meaning of results. Sampling presents difficult problems, since however carefully objects (men, dogs, etc.) are classified, there are still innumerable differences between the individual members of a group of objects. Any conclusions drawn about the group as a whole are therefore open to the objection that attention may not have been paid to some relevant differences between individuals. Homogeneous samples and identical objects are rare in biological science.

A further difference between the physical and biological sciences is that, in the former, phenomena are relatively simple ; causes and effects are few, controls are easy to devise, and it is therefore relatively easy to disentangle causes and effects. In the biological sciences, however, phenomena are much more complex ; causes and effects are so numerous that it is often impossible to carry out strict controls and the disentangling of causes and effects is vastly more difficult. There is the additional limitation that if life must be maintained, drastic variations in certain conditions of experiment are not permissible.

FURTHER READING

This list of books covers Chapters 1, 2 and 3.

GENERAL

PEARSON, K. The Grammar of Science, 2nd edition. Black, London, 1900.

RITCHIE, A. D. Scientific Method. Kegan Paul, Trench and Trubner, London, 1923.

WESTAWAY, F. W. Scientific Method—Its Philosophy and Practice, 4th edition. Blackie, London, 1931.

MISCELLANEOUS

FREUND, IDA. The Study of Chemical Composition. Cambridge University Press, Cambridge, 1904. (Out of print.)
     The introduction deals with the method of the inductive sciences. The rest of the book is most valuable for the historical study of general chemistry.

FREUND, IDA. The Experimental Basis of Chemistry. Cambridge University Press, Cambridge, 1920.
     The introduction considers the true nature of students' practical work. The rest of the book is most valuable for experiments illustrating the fundamental principles of chemistry.

FISHER, R. A. The Design of Experiments, 3rd edition. Oliver and Boyd, Edinburgh, 1942.
     (Advanced.)

TUTTLE, L., and SATTERLY, J. The Theory of Experiments. Longmans, Green, London, 1925.

STATISTICAL METHOD

BRADFORD HILL, A. Principles of Medical Statistics, 3rd edition. The Lancet, London, 1942.

CHAMBERS, E. G. Statistical Calculation for Beginners. Cambridge University Press, Cambridge, 1940.

FISHER, R. A. Statistical Methods for Research Workers, 9th edition. Oliver and Boyd, Edinburgh, 1944.

GENERAL IDEAS
ON QUALITATIVE WORK

In any science, qualitative work, *i.e.*, the study of the *kind* of material present, precedes quantitative work, *i.e.*, the study of the *amount* of material present. Some aspects of qualitative work involve quantitative considerations (*e.g.*, the measurements involved in the proof of identity and purity; sensitivity of tests, p. 12).

2, 1   THE IDENTITY OF SUBSTANCES

Two substances (A and B) are considered identical if for every property of the substances which has been measured, the value for A is (within the limits of experimental error) identical with the value for B. For a complete proof of identity, every known property should be measured. Such an ideal comparison is never made because of the time that would be required.

In practice, comparison is restricted to a few selected properties, *e.g.*, melting-point, boiling-point, refractive index, density, optical rotation, solubilities. Even if two substances are identical in all these properties, the discovery of a difference in any other property is sufficient to prove that the substances are *not* identical.

2, 2   THE PURITY OF A SUBSTANCE

A substance is considered pure if it fulfils the following conditions :

1. It is homogeneous, *i.e.*, all parts of it are identical in all properties.

2. If any change is made in the physical conditions, the substance *either* remains wholly unchanged *or* changes wholly in the same way (*e.g.*, on heating, it all melts at the same temperature, or all boils at the same temperature).

3. If the substance is treated with other materials (*i.e.*, is given the chance to undergo chemical change) it *either* remains wholly unchanged *or* changes wholly in the same way.[1]

For a complete proof of purity, the substance would have to be submitted to every possible change in physical conditions and to every possible treatment with other materials. Such an ideal proof is impossible due to lack of time, and in practice, examination is confined

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[1] In reactions where an equilibrium mixture is formed, it is necessary to remove the reaction products, so as to give the whole of the substance a fair chance to react in the same way.

TUTTLE, L., and SATTERLY, J. The Theory of Experiments. Longmans, Green, London, 1925.

STATISTICAL METHOD

BRADFORD HILL, A. Principles of Medical Statistics, 3rd edition. The Lancet, London, 1942.

CHAMBERS, E. G. Statistical Calculation for Beginners. Cambridge University Press, Cambridge, 1940. ·

FISHER, R. A. Statistical Methods for Research Workers, 9th edition. Oliver and Boyd, Edinburgh, 1944.

Test   I. Positive result with A, B, C.   Negative result with all
                                                       other substances.
Test II. ·   „   „   D, E, F, G.   „   „
Test III.   „   „   H, J.   „   „

When the groups present have been determined thus, *specific* tests
are used to decide which members of each group are present. If, *e.g.*,
group ABC has been found present, tests specific for A, for B and for
C must be applied.

In medicine the mental processes used in making a diagnosis are
similar to, but unfortunately can rarely be as precise as, those outlined
above.

Attention must be drawn to a special arrangement found in the
usual method for cation (or metallic radical) analysis. Here a series
of group tests is used, each of which gives a positive result with the
cations of its own group *and with most of the cations of preceding groups*.
The first group reagent, hydrochloric acid, gives a precipitate only
with silver, lead and mercurous cations. These are called Group 1.
The second group reagent, hydrogen sulphide in acid solution, gives a
precipitate with copper, bismuth, mercuric, cadmium, arsenic, anti-
mony, tin and the three cations of Group 1. The cations just named
from copper to tin inclusive are called Group 2. It must be clearly
understood that Group 2 is defined, *not* as "Cations which give a
precipitate with hydrogen sulphide in acid solution," but as "Cations
which give a precipitate with hydrogen sulphide in acid solution, but
which do *not* give a precipitate with hydrochloric acid."

The order in which the group tests are done therefore affects the
conclusions to be drawn from the results. If the usual order is followed,
the tests, observations and conclusions in a certain case might be
summarised as follows :

Test	Observation	Conclusion
Solution of substance +HCl.	No ppt. formed.	Cations of Group 1 absent.
Solution of substance +HCl and H_2S.	Ppt. formed.	Cations of Group 2 present.

If, however, the test with hydrogen sulphide and acid is done first,
the conclusions to be drawn from the formation of a precipitate are
quite different, thus :

Test	Observation	Conclusion
Solution of substance +HCl and H_2S.	Ppt. formed.	Cations of Group 1 and/or Group 2 present.

to the more obvious criteria of purity, *e.g.*, determination of melting-point, boiling-point and a few other physical properties; and examination of the behaviour of a specimen with reagents that are known to give a visible reaction with likely impurities.

It is important to note that all " proofs " of identity and purity are essentially *negative*. It is never possible to say with certainty " These two substances are identical " or " This substance is pure." It is possible only to say " In all the tests to which they have so far been submitted, these two substances have shown no differences in properties " or " In all the tests to which it has so far been submitted, this substance has remained wholly unchanged, or has changed wholly in the same way."

2, 3   SPECIFIC TESTS AND GROUP TESTS

In qualitative analysis of any kind—in chemistry, in clinical diagnosis, in the investigation of the reason why a motor car will not go—tests may be of two kinds, viz., specific tests and group tests.

Specific Tests are tests in which a positive result is given by only one substance or condition (*e.g.*, the formation of a white precipitate with barium nitrate in acid solution, given only by sulphate ions). Specific tests are rare.

Group Tests are tests in which a positive result is given by two or more substances or conditions (*e.g.*, the formation of a white precipitate with hydrochloric acid, given by mercurous, silver and lead ions). The positive results may be of different kinds, *e.g.*, precipitates of different colours.

Before a test is of any value, the behaviour of *every* substance which might be present in the material under examination must be known. There is a great difference between *knowing that nothing happens* in certain circumstances, and *not knowing what happens* in those circumstances.

Emphasis has been laid on this principle throughout this book; in the chapters dealing with ions and with organic radicals, the behaviour of every ion or radical towards the general analytical reagents has been described.

2, 4   THE LOGIC OF ANALYSIS

Given specific and group tests sufficient to distinguish a number of substances or conditions A, B, C, D, etc., there are many ways of combining the tests to perform an analysis. The ideal arrangement is that which takes the least time. It may be possible to choose a series of tests, each specific for one substance, but this method is lengthy and often impossible. The commonest method is to choose a number of *group* tests, each of which indicates whether or not any member of a little group of substances or conditions is present, thus *e.g.*,

Test   I. Positive result with A, B, C.   Negative result with all
                                                    other substances.
Test II.   ,,   ,,   D, E, F, G.   ,,   ,,
Test III.   ,,   ,,   H, J.   ,,   ,,

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GENERAL IDEAS
ON QUANTITATIVE WORK

3, 1   MEASUREMENT

Physical measurements are of two kinds, first the simple process of counting separate objects (*e.g.*, men, guinea-pigs, weights), and secondly the measurement of properties which are continuously variable (*e.g.*, length, volume, time). By counting separate objects, it is obviously possible to learn the exact number of objects present. The measurement of a continuously variable property, however, can never determine the " absolute " value of the property, but only the *limits* within which the value lies. The more accurate the measurement, the closer to one another are these limits. The remainder of this section deals solely with measurements of the second type.
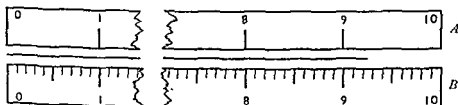
FIG. 3, 1

Measurement

Suppose the length of a straight line is measured with a ruler marked only in centimetres (see Fig. 3, 1, *A*). Suppose that if the o mark of the ruler is placed against the left-hand end of the line, the right-hand end of the line comes somewhere between the 9 cm. and 10 cm. mark and nearer to the 9 cm. mark. It can then be stated that " The length of the line is 9 cm.," which means, " The length of the line is nearer to 9 cm. than to 8 cm. or 10 cm., *i.e.*, it is between 8·5 and 9·5 cm." It is possible to estimate by eye the number of tenths of a centimetre by which the length of the line exceeds 9 cm. Suppose this number is 3. It can then be stated that " The length of the line is 9·3 cm." Complete confidence cannot, however, be placed in the figure 3, as it can in the figure 9.

Next suppose that a ruler graduated in centimetres and tenths of a centimetre (millimetres) is used (Fig. 3, 1, *B*); suppose the right-hand end of the line comes between the 9·2 cm. and 9·3 cm. mark, and nearer to the 9·3 mark. It can now be stated with certainty that " The length of the line is 9·3 cm.," which means, " The length of the

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Subsequent group reagents similarly precipitate nearly all the cations in the preceding groups.

It will thus be seen that the group tests must always be carried out in the usual order, since this is not a matter of casual choice, but part of a carefully thought-out plan. The example above illustrates well the importance of negative evidence.

Order is likewise of great importance in clinical examination, and physical diagnosis is facilitated by employing the methods available in an orderly way.

2, 5   CONTROL TESTS

It is often difficult to tell at a glance whether the visible result in a test (*e.g.*, the formation of a colour) is due to the substance which the test is intended to detect, or to the testing materials themselves. In such cases it is necessary to carry out positive and negative control tests, *i.e.*, to see what visible result, if any, is obtained when the test is carried out in precisely the same way (1) with an authentic sample of the substance to be detected (*positive control*), and (2) in the certain absence of the substance to be detected (*negative control* or *blank test*). The value of this procedure, which must be adopted in all cases of doubt, cannot be too strongly emphasised.

The comparison of a limb in which injury or abnormality is suspected, with the opposite limb, which should be normal, is an excellent clinical example of a control test.

2, 6   SENSITIVITY OF TESTS

Each test will detect a particular substance, *i.e.*, give a visible reaction, only if the substance is present in a quantity or concentration not less than a certain minimum, which is called the *sensitivity* of the test.

A rough knowledge of the sensitivity of every test used is necessary, since without it the analyst may be seriously misled. On the one hand if he relies on tests which have a very low sensitivity (*i.e.*, in which high concentration is necessary to give a positive result), he may allow a substance to escape detection, whereas a more sensitive test would have detected its presence.

On the other hand, the use of very sensitive tests (*e.g.*, the flame test for sodium) may lead the analyst to confuse substances present only in minute traces with major constituents of the material under examination. The sensitivity of most precipitation reactions used in inorganic qualitative analysis is such that the ions can be detected by the methods used here in minimum concentrations of approximately 10^{-3} M. Some colour tests give positive reactions with various inorganic ions in minimum concentrations of approximately 10^{-5} M or 10^{-6} M.

FURTHER READING

See the list of books on pp. 7-8.

To sum up what has been said in this section and the preceding one:

1. No measurement is absolutely accurate.

2. A statement of a measurement must include or imply a statement of its accuracy.

3. The usual convention in stating measurements is to give all the significant figures which have been determined with certainty and one further estimated figure.

3, 3   REPETITION OF MEASUREMENTS

If any quantity is measured a number of times, the results are rarely identical. While it is understood that the result can never be known with absolute accuracy, it is necessary to ask " What are the *limits* between which the quantity must lie ? ", and it is desirable to ask " How can these limits be narrowed so that we can know the value more accurately ? "

The differences between results arise from three sources, viz. :

1. *Mistakes*—due to lack of care in a single determination.

2. *Constant Errors*—due to inaccuracies in apparatus, material or manipulation, which affect equally all members of a series of determinations.

3. *Random Variations*—due to the fact that however carefully apparatus is constructed and handled, repeated determinations do not give identical results.

Before these three sources of difference are considered it must be pointed out that differences in results are most conveniently expressed as *percentages* of the quantity measured. If, for example, the results for a series of titrations are 10·15, 10·13, 10·16, 10·14, 10·17, 10·15 ml., the average is 10·15 ml., and the range is ±0·02 ml. or ±0·2%. If the results are 1·05, 1·03, 1·06, 1·04, 1·07, 1·05 ml., the average is 1·05 ml., and the range ±0·02 ml. or ±2%.

The terms " accuracy " and " precision " are often confused. The *accuracy* of a result is a measure of the difference between that result and the true result, when the latter can be determined in some other way. The *precision* of a series of results is a measure of the random variation between them without reference to the true result.

3, 4   MISTAKES

Mistakes are easy to detect, easy to correct and easy to avoid. The most careful and experienced worker is, however, liable to make mistakes, and the possibility of their occurrence must never be overlooked.

Mistakes can occur through lack of care in any of the following operations :

1. Manipulation (*e.g.*, spilling liquid from a pipette on to the bench,

line is nearer to 9·3 cm. than to 9·2 or 9·4 cm., or somewhere between 9·25 and 9·35 cm." Again tenths of a graduation could be estimated by eye. Thus in the example given it might be stated that " The length of the line is 9·28 cm."; once again the estimated figure 8

to x graduations," meaning that it is nearer to x than it is to $x+1$ or $x-1$ and (2) " The length is *probably* equal to x graduations + y fractions of a graduation, which have been estimated by eye."

The above applies to any ordinary graduated scale, *e.g.*, on a burette, pipette, thermometer, watch or balance. An aid to accuracy in reading, which will be met more frequently in practical physics than in chemistry, is the Vernier Scale (for details see, *e.g.*, Crowther, *A Manual of Physics*, Oxford University Press, 4th edition, 1936, p. 3).

3, 2   MEANING OF FIGURES

Since no measurement is accurate in the absolute sense, any statement of the result of a measurement should state its accuracy. A simple but inconvenient way to do this is to state the limits within which the quantity lies, *e.g.*, for the example in Fig. 3, 1, A, " Between 8·5 cm. and 9·5 cm." A more convenient way is to state the middle-point of the range and the range, thus " 9±0·5 cm." In most measurements, fractions of a graduation have been estimated as discussed above. It is customary to give results to such a number of figures

and 9·28$_5$ cm. One way of showing that a last digit is doubtful is by writing it in small type rather lower than the " certain " digits thus, 9·2$_8$. This method is rarely used because of inconvenience in printing.

The accuracy of a measurement is indicated by the number of *significant figures* with which the result is expressed. The significant figures of a number are all the digits, except o's placed at the beginning or end of the number to locate the decimal point. Thus 93, 9·3 and 0·000093 each have two significant figures.

Note the difference between

8   ml., which means anything between 7·5   and 8·5   ml.
8·0   ml.,   „   „   „   „   7·95   „   8·05   ml.
8·00 ml.,   „   „   „   „   7·995   „   8·005 ml.

The o's in 8·0 and 8·00 *are* significant figures. If a burette is read to two places of decimals, and the bottom of the meniscus is exactly on the 8 mark, the reading *must* be reported as " 8·00 ml." If it is reported as " 8 ml.," anyone reading the notes will assume that the volume was only measured to the nearest millilitre.

variation. The reason for the variation could be tracked down by comparing A's and B's procedures with the standard procedure for every operation involved. It might be found that B, although always handling his pipette in the same way, was handling it in a way different from the accepted fashion on which the calibration was based. The remedy is obvious.

Errors of the types discussed above are called *constant errors*, and are sometimes further classified as apparatus, reagent and personal errors.

Many analytical methods involve constant errors due to imperfections in the method, unavoidable impurities in reagents, etc. Allowance for these constant errors may be made in one of the following ways :

1. The method is carried out on one or more samples containing *none* of the material to be determined. The average result of these " blank tests " is then subtracted from all other results obtained with the same batches of reagents.

2. The method is carried out on a series of samples containing different known quantities of the substance to be determined, and a curve drawn relating results to quantities present. The results obtained subsequently with unknown samples can then be interpreted by means of this curve.

3, 6   RANDOM VARIATIONS

Random variations are those which cannot be avoided however carefully an operation is repeated with the best apparatus.

The causes of these random variations are to be found at every stage of an operation. Consider the act of pipetting samples from a beaker of stock solution into a conical flask. The following are some causes of variation in the volumes of liquid [1] transferred, even when the work is done as carefully as possible :

1. Difference in the position of the meniscus at the mark.

2. Difference in the volume of the drop hanging from the tip of the pipette.

3. Difference in the volume of liquid adhering to the outside of the pipette.

4. Difference in the speed of drainage depending on the position in which the pipette is held for delivery.

5. Difference in the time allowed for drainage after the meniscus has reached the tip.

6. Difference in the way the pipette is withdrawn from the flask into which it has delivered.

In a complete titration, similar causes of random variation arise in the handling of the burette, and a further cause lies in the uncertainty of even the sharpest end-point colour change.

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[1] These volumes can be determined by weighing the flask after each addition, the density of the liquid being known.

when it should have been put into the titration-flask ; failing to make a standard solution homogeneous).

2. *Observation* (*e.g.*, observing a volume as 10·8 ml., when it is really 9·8 ml.).

3. *Recording* (*e.g.*, recording a weight as 12·7 g. through carelessness in addition, when the weights total 12·8 g.).

Mistakes of all kinds can be detected by carrying out at least two determinations of any quantity, and *reliance should never be placed on a single determination, unless this is unavoidable.* If two determinations of a quantity do not agree within the limits of random variation (see pp. 17–18), it is *certain* that a mistake has been made.. The mistake can be corrected only by further determinations.

Mistakes can be avoided by constant care in manipulation, observation and recording.

3, 5   CONSTANT ERRORS

Determinations may agree amongst themselves within the limits of random variation, and yet all be wrong.

Suppose two series of titrations are done by the same worker with the same solutions and the same burette, but with two different pipettes X and Y each reputed to deliver 10·00 ml. Suppose the results obtained are as follows :

Using pipette X.   10·15, 10·13, 10·14, 10·17, 10·15 ml.
             i.e., 10·15±0·02 ml..

Using pipette Y.   10·23, 10·26, 10·23, 10·25, 10·27 ml.
             i.e., 10·25±0·02 ml.

It is obvious that Y is delivering more liquid than X. The only ways in which the worker can decide whether X or Y (or both) are inaccurate are :

1, calibrating X and Y, *i.e.*, checking them against known standards (see p. 21) ;

2, carrying out the titrations with another pipette Z, which is known to deliver the correct volume.

Secondly, suppose two sets of titrations are done by the same worker with the same burette and pipette using a standard acid solution P in both sets, but using two different alkali solutions Q_1 and Q_2, reputed to be of identical normality.

If results for the set of titrations with Q_1 differ from those with Q_2 by more than the random variation, it is clear that one or both of the solutions Q_1 and Q_2 is inaccurate. The remedy is to prepare another · alkali solution Q_3 of known normality and carry out the titrations with this.

Thirdly, suppose two sets of titrations with the same solutions and same sets of apparatus are done by two different workers, A and B, and suppose A's results differ from B's by more than the random

The statistician has many measures of the spread or scatter of results about the mean; the most important of these is called the Standard Deviation, which indicates the proportion of the results lying between given values on either side of the mean.

2. *The Deduction of the best possible Estimate of a Physical Magnitude from Experimental Data.*

In the case considered above, every possible individual measurement was made. In nearly all scientific work, observations are made only on one or more samples drawn from the whole amount of material (population) whose properties are under examination. This applies both to the biological scientist choosing, say, 5% of the 10-year-old boys in each Edinburgh school to measure their heights, and to the physical scientist taking several different samples of a material for analysis. Even if the samples are true random samples in each case —and it is much more difficult for the biologist than for the chemist or physicist to ensure this—the means of the observations for the samples will not be the same as the mean for the whole population. The statistician gives his estimate of the true mean in terms of the observed mean and the Standard Error, which is a function of the Standard Deviation and the number of observations. If the observed mean is X and the Standard Error is SE, then the probability is 19 : 1 that the true mean of the whole population lies between the limits X±2SE. An example of the use of the Standard Error in interpreting results is given in the following paragraph.

3. *Tests of Significance.*

Results obtained in different conditions may be compared to see whether there is any significance (*i.e.*, any real meaning) in the differences between them, or whether these differences are such as might be found between two random samples drawn from the same populations. Suppose a number of cases of a certain disease are under examination. The signs of the disease, *i.e.*, the ways in which diseased persons differ from normal persons, are noted. The differences may be such as can only be detected qualitatively. It may, however, be found that diseased persons appear to differ from normal persons in certain characteristics (*e.g.*, blood sugar concentration) that can be measured quantitatively. The hypothesis that this particular disease and blood sugar concentration have some connection with one another is formulated and then tested. Suppose blood sugar determinations for diseased[1] persons give the following results : 175, 171, 190, 182, 182, 185, 193, 169, 184, 187 mg. per 100 ml. (mean=181·8 mg. per 100 ml.) whereas those for normal[1] persons give the results : 79, 82, 89, 91, 81, 82, 90, 85, 86, 84 mg. per 100 ml. (mean=84·9 mg. per 100 ml.):

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[1] It is presumed throughout this argument that the samples both of diseased persons and of normal persons (the controls) are true random samples, *i.e.*, that all other possible interfering factors have been removed.

The question now arises, " Granted that some random variation is inevitable, within what limits is the true result likely to lie ? " This and other related questions on the interpretation of results are the business of statistical method, which is briefly considered in the following section.

Random variations may be reduced by improvements in the design of apparatus, and still more by consistent and careful manipulation. Since the factor of real significance is the ratio of the random variation to the quantity measured, it is useless to increase the quantity measured if the random variation is increased in the same proportion.

3, 7   STATISTICAL METHOD

It has been shown in the preceding section that even if all mistakes and constant errors are avoided, a series of determinations of the same property in physical science rarely give identical answers, on account of imperfections in apparatus and manipulation. It has also been pointed out (pp. 6–7) that the biological scientist studying similar but non-identical objects nearly always obtains varying results for his measurements.

In both types of work the individual observations are of little value. What are wanted are general truths about the whole of the material from which the samples have been drawn. The question arises, " What general information can be obtained from a given collection of data ? " It is the business of statistical method to answer this question. While the physical scientist is in practice often able to manage without making much use of statistical methods, the biological scientist doing quantitative work always needs them.

The machinery of statistical method, which is based on the mathematical laws of chance or probability, is not described here. The simpler parts of it must, however, be studied by anyone who wishes to work with quantitative data of any kind (e.g., mortality, efficacy of treatment, variations from normal in physiological data) and references to elementary books on the subject are given on p. 8. The following are some of the tasks which statistical method helps to accomplish:

1. The Reduction of a large Mass of Data to a few Figures.

Suppose the heights of all boys aged 10 in Edinburgh schools are measured. The results, about 3500 observations in all, are a mass of data from which it is impossible to get any useful impression about the average boy. If, however, the arithmetic mean of all the observations (say 4 ft. 6 in.) is found, it gives an easily comprehensible idea of the height of an average 10-year-old Edinburgh schoolboy. This figure alone does not indicate how the individual heights are scattered about the mean; it would not distinguish between the case in which, e.g., 99% of the heights are between 4 ft. 5 in. and 4 ft. 7 in., and that in which, e.g., they are spread evenly between 4 ft. 0 in. and 5 ft. 0 in.

3, 8   CALIBRATION

Measuring instruments like all other materials are open to suspicion, and no measuring instrument should be used until its maker's claims have been tested.[1]   The testing of measuring instruments is called calibration;   it involves the use of other standard instruments or materials whose accuracy or purity is known.   Transfer pipettes, for example, may be calibrated by weighing on a balance the water delivered by the pipette, and calculating from that weight and from the accepted value for the density of water the volume of water delivered. The accuracy of the pipette is then dependent on

    1. the accuracy of the balance used,
    2. the accuracy of the weights used,
    3. the purity of the water used,
    4. the accuracy of the accepted value for the density of water.

The standard instruments and materials must in their turn have been calibrated against others.   Ultimately comparison must be made with the arbitrary world standards, *e.g.*, those of mass and length, which are (or were) kept in Paris.

The most convenient way of obtaining apparatus of . is to buy apparatus which has been . . . Laboratory (NPL), Teddington, Middl for some volumetric apparatus are given in Chapter 5, p. 60.   Full details of NPL standards and tests are contained in a series of Test Pamphlets which may be obtained from the Director.

3, 9   CALCULATIONS

The accuracy of a result depends primarily on that of the " weakest link " in the work, *i.e.*, on that of the *least accurate* observations involved.   It is dishonest to state a result in such a way as to imply an accuracy which the observations do not warrant.

As already stated (pp. 13–14), observations are usually reported with one uncertain figure, *e.g.*, in reading a burette graduated in 0·1 ml., volumes are estimated to the nearest tenth of a division and the readings reported to 0·01 ml.

In *addition* or *subtraction*, the result must have the same number of places of decimals as the least accurate observation.   Consider, for example, the addition of three weights:

$$\begin{array}{r} 10\cdot70 \ \text{g.} \\ 1\cdot004 \ \text{g.} \\ 0\cdot0079 \ \text{g.} \end{array}$$

These add arithmetically to 11·7119 g.   This figure implies that all weights were determined to the nearest 0·0001 g.   In fact, the least

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[1] This policy cannot be followed in students' elementary work because of the time involved, but it must be followed in more advanced work and in research.

no statistical method is necessary to make it obvious that the disease is associated with (but not necessarily caused by) high blood sugar concentration, because the whole range of " diseased " values is well clear of the range of normal values, and the " diseased " mean is about twice the " normal " mean. Usually, however, the problem is much less simple. Suppose the figures are for " normals " as above, and for " diseased " 92, 97, 85, 94, 91, 83, 99, 87, 88, 91 mg. per 100 ml. (mean = 90·7 mg. per 100 ml.). If someone states baldly, " The average blood sugar concentration for ' normals ' is 84·9, while the average blood sugar concentration for ' diseased ' is 90·7 ; therefore high blood sugar is associated with this disease," the result looks impressive until it is asked, " How do the values vary from one individual to another among normal persons, and among diseased persons ? " Once the actual observations are quoted, it is seen that the results as they stand convey nothing. The Standard Errors must be worked out, and then statistical tables can be consulted to see whether the results are significant, i.e., whether or not the difference between the " normal " mean and the " diseased " mean is one that would occur more than 1 in 20 times [1] between two normal random samples. If the difference between the two means is by the laws of chance likely to occur more than 1 in 20 times between two different normal samples, then the claim that the disease is associated with high blood sugar is unfounded. If, on the other hand, the difference between the two means is such as would occur less frequently than 1 in 20 times between two normal samples, it may be claimed that this disease and high blood sugar concentration are associated. The fact that there is a statistically real association does not, however, prove a cause-and-effect relationship.

4. The Calculation of Correlations.

In many cases where a cause-and-effect relationship between two factors is suspected, both factors concerned can be measured quantitatively (e.g., age and incidence of a disease). Statistical method will determine what degree of correlation (positive, negative or none) there is between the two factors. In the example given it will determine whether there is a significant increase (or decrease) in the incidence of the disease with increasing age, or whether there is no correlation at all between age and incidence.

5. The Design of Experiments.

It has been pointed out (p. 4) that if experiments are to give results of real value, their number and kind must fulfil the requirements indicated by statistical method. To put this in another way, the planning and the interpretation of experiments are two aspects of the same thing.

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[1] This figure, 1 in 20, is an arbitrary choice, which has been proved satisfactory by experience.

PRACTICAL METHODS

The chemist's work consists chiefly in trying to make substances react, and to separate the products when substances have reacted. Since he cannot handle individual molecules, he cannot make individual molecules react, or separate the individual molecules of the new substances produced. All that he can do is to manipulate apparatus in such a way as to give the molecules a *chance* to react or to separate. The only methods of giving molecules a chance to react are physical methods, *e.g.*, mixing them, heating or cooling them, passing an electric current through them. The only methods of giving molecules of different kinds a chance to separate are physical methods, *e.g.*, filtration, use of the separating funnel, distillation, freezing. Since the methods involved in both types of work are physical, the laboratory operations of chemistry depend essentially on the physical characteristics and above all on the states (gaseous, liquid or solid) of the substances concerned.

Chapter 4 deals with manipulation in general. Chapter 5 deals with manipulation in which measurement is carried out.

CHAPTER 4

MANIPULATION

4, 1   GENERAL RULES FOR LABORATORY WORK

1. Before you carry out any operation, know what you want to do, and why you want to do it; choose your apparatus and materials accordingly.

2. Use clean apparatus and reliable [1] materials. Work with dirty apparatus and unreliable materials is worthless.

3. Understand what your apparatus will and will not do.

4. Arrange your apparatus so that all operations and observations can be carried out with a minimum of trouble, in order to get the best out of the apparatus and your powers of observation. This is not pandering to laziness; it is common-sense.

5. Wipe your bench clean with a duster before you start work and after you have finished work each day. Keep your bench clean and tidy while working. If material is spilt, clean it up at once.

6. Store apparatus and materials in an orderly fashion so that they remain clean and are not easily broken.

7. Remember that by chemical standards your hands are always dirty.

[1] " Reliable materials " mean " Materials known not to contain impurities likely to interfere with the work in hand."

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accurate was only determined to the nearest 0·01 g. The total must therefore be given to the nearest 0·01 g. thus :

$$10·70 \text{ g.}$$
$$1·00 \text{ g.}$$
$$0·01 \text{ g. *}$$
$$\overline{11·71 \text{ g.}}$$

* If the first figure rejected is 5 or over, add one to the last figure retained.

This total, 11·71 g., is a fair statement of the truth.

In *multiplication* or *division*, the result must contain the same number of significant figures as the factor having the smallest number of significant figures. Suppose, for example, the following result was obtained in a titration :

10·00 ml. of solution " X "=10·32 ml. of 0·107N solution " Y."

Normality of " X " = $\dfrac{10·32 \times 0·107}{10·00}$.

If this fraction is worked out as an exercise in arithmetic, the answer is 0·110424N. To give a fair statement of the truth, however, the answer must be expressed as 0·110N.

FURTHER READING

See the list of books on pp. 7–8.

2. If apparatus appears dirty after six rinsings with tap water, scrub with a brush and soft soap or Vim, and then carry out method 1.

3. If soap or Vim and water treatment is not successful, fill the vessel [1] with hot chromic acid cleaning mixture, heat gently for half an hour, pour the cleaning mixture into the stock-bottle for re-use and carry out method 1. (Take care *not* to spill the cleaning mixture, which is a solution of potassium dichromate in concentrated sulphuric acid, on your hands or clothes.)

4. When a vessel has contained a solution in a non-aqueous solvent, it is often worth while to wash it out two or three times with small volumes of this solvent before trying method 1.

In all cases pay particular attention to the invisible parts of apparatus (*e.g.*, of porcelain filter-funnels), and to lips and rims over which liquid is poured.

Criteria of Cleanliness.

1. Apparatus cannot be clean if it does not look clean. However, even if it looks clean, it is not necessarily clean.

2. If water tends to form drops on any part of the vessel, the latter is greasy and needs further attention.

3. Dirt on the outside of a vessel may not matter in itself, but if it is there the cleanliness of the inside cannot be judged.

4. If unexpected results cannot be explained otherwise, suspect the apparatus of being dirty, no matter how carefully it has been cleaned.

Drying.

The methods available are simple draining (slow), hot oven (quick), or rinsing with alcohol followed by ether or else acetone (quick ; the last traces of solvent are removed with the air-blast in the absence of naked flames).

Do *not* wipe the inside of any vessel with a cloth, however clean the latter appears.

RUBBER STOPPERS

Wash with water or with the solvent previously used. Wipe over with acetone occasionally to remove adhering dirt.

CORKS

These should be used only once and then rejected. To save expense in elementary work, however, they may be washed with water, allowed to dry and used again.

SUPPORTS FOR APPARATUS

Stands, clamps, bosses, etc., should be kept dry and free from dust. Grease the screws occasionally.

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[1] Volumetric apparatus must *not* be heated. To clean this, fill it with cold chromic acid-nitric acid cleaning mixture and leave to stand overnight.

8. Do *not* insert into a reagent bottle anything (*e.g.*, glass rod, pipette, spatula) which may contaminate the contents.

9. When taking liquid from bottles use the method described on pp. 27-28.

10. Do *not* remove from their proper places bottles which are intended for other people's use as well as your own.

11. Pour waste liquids down the sink with much water.

12. Put solid rubbish in the receptacles provided, *not* in the sinks.

13. Label any material which has to be left from one day to another. If it is not left in your own locker, put your name on it.

14. Use the quantities of materials stated in the instructions, *not* twice or three times as much. The experiments have all been tested with the quantities stated here, and the use of larger quantities is sheer waste. See pp. 443-444 regarding rough measurement.

15. Whenever water is mentioned in instructions, use *distilled* water unless tap water is specially mentioned.

16. If a solution has to be made acid, alkaline or neutral, only an indicator will show when the desired result has been achieved. It is no good just adding " a lot of acid " and hoping for the best.

DANGER WARNINGS

17. Do *not* try any experiment which you have not been told to do without first consulting a demonstrator.

18. Do *not* taste anything in the laboratory. Do *not* lick labels.

19. Do *not* fill a test-tube, which has to be heated, more than one-third full of liquid.

20. Do *not* heat a test-tube containing liquid without shaking it during heating.

21. When a test-tube is being heated—and particularly when it contains concentrated acid or alkali—point it so that the contents cannot spurt over your neighbours or yourself.

22. Do *not* smell the contents of a hot test-tube by holding your face over it.

23. Do *not* pour hot concentrated sulphuric acid into water. Never pour water into concentrated sulphuric acid.

24. Remember that nearly all organic liquids and their vapours are inflammable. Do not therefore bring them near naked lights.

25.   ' (see p. 30), turn it out *at once*.

26.   our hands or clothes. Always wash your hands thoroughly before leaving the laboratory.

4, 2   CLEANING OF APPARATUS

GLASS AND PORCELAIN

All apparatus should be cleaned as soon as possible after use.

Methods of Cleaning.

1. Rinse six times under the tap, rinse twice with distilled water and leave to drain.

Evolution of Gases.

Two types of gas producer are used, viz. :

A. Used when gas is evolved from a solid reagent or reagents on heating.

B. Used when gas is evolved from a liquid or liquid and solid, with or without heating.

Collection of Gases.

The gases are collected in test-tubes or boiling-tubes which are corked when full.

With each type of gas producer three arrangements for collection are possible, viz. :

1. *Collection over water.* Used when the gas is sparingly soluble in water (sometimes hot water may be necessary).

2. *Collection by upward displacement of air.* Used for gases which are appreciably denser than air.

3. *Collection by downward displacement of air.* Used for gases which are appreciably less dense than air.

Drying of Gases.

Gases may be dried if necessary by means of a filter-tube arranged as a gas wash-bottle (Fig. 4, 1, C) containing a suitable dehydrating agent.

Points to Note.

1. In *A*, the test-tube is sloped downwards slightly towards the cork so that if moisture condenses it does not run into the hot part of the tube. The reagents are spread in a thin layer along the bottom of the tube and heating is started at the end nearest the cork.

2. In *B* the lower end of the straight vertical safety tube is below the surface of the liquid.

3. In all cases, make sure that air has been driven out of the apparatus before collecting the gas.

4. When collecting over water, do not allow water to " suck back " into the heated apparatus.

4, 4   TRANSFER OF LIQUIDS

Transfer without Measurement

An approximate volume of liquid can be transferred from one vessel to another by pouring.

Use of a Reagent Bottle.

1. If the vessel into which you wish to pour the liquid will not stand up by itself, hold it between the thumb and forefinger of the left hand.

2. Hold

3. Remov

finger and palm of the left hand.

TRANSFER OF MATERIALS

4, 3   TRANSFER OF GASES

A gas will transfer part of itself to any space to which it has access. It is therefore necessary only to provide a closed path from the point where a gas is being evolved (*e.g.*, in a preparation, test or distillation) to the point where it is desired to collect the gas (gas-jar, test-tube containing reagent, or condenser).

Preparation and Collection of Gases

The common gases may be prepared and collected in very simple apparatus constructed from test-tubes, boiling-tubes and bent glass tubing as illustrated in Fig. 4, 1.
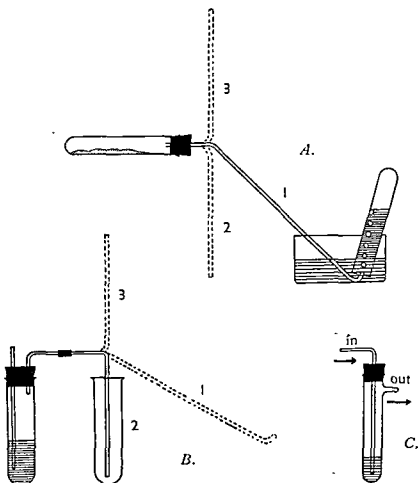
Fig. 4, 1

Apparatus for Preparation and Collection of Gases

4, 5   **TRANSFER OF SOLIDS**

Part of a given quantity of solid may be transferred from one vessel A to another B by shaking or by means of a *clean* spatula. If B has a narrow neck it is often convenient to shake the solid on to a clean piece of glazed paper or a watch-glass, and transfer it from this to B with a spatula. The same method may be used to transfer the *whole* of a given quantity of solid from A to B in rough work.

When it is necessary in accurate work to transfer the *whole* of a solid from one vessel to another, the solid is usually brought into solution; the problem is then that of transferring the whole of a liquid sample (see p. 28).

HEATING AND COOLING

4, 6   **THE BUNSEN BURNER**

The simplest method of heating is direct heating by a Bunsen burner (Fig. 4, 3). Glass or porcelain vessels (other than test-tubes) are supported by a wire gauze on a tripod over the burner.

The type of flame produced by the burner is determined by the amount of air admitted by the control ring C, which has a hole in it. If the control ring C is adjusted so that the hole is *not* opposite the hole A in the side of the Bunsen tube T, no air is admitted; the flame is luminous and is not very hot. A small luminous flame is used for charcoal block tests with the blowpipe (see p. 185) and sometimes for melting-point determinations (see pp. 65-66). If C is adjusted so that a little air is admitted through the opening A, a pale mauve non-luminous flame is produced. Such a flame, about $1\frac{1}{2}$ in. high, is sufficient for most test-tube reactions. If C is adjusted so that its hole coincides with A, the maximum amount of air is admitted and a very hot flame of the structure shown in Fig. 4, 3 is produced.

The parts of the non-luminous Bunsen flame shown in Fig. 4, 3 are as follows :

B—Inner cone (blue) ; unburnt gas.

L—Luminous tip of the inner cone (light blue) ; gas burning partially in air ; reducing flame.

M—Outer mantle (mauve) ; gas burning completely in air ; oxidising flame.
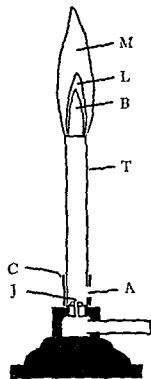
FIG. 4, 3
Bunsen Burner

Smaller burners of Bunsen type are often used for micro-work. A blowpipe makes a very useful micro-burner (*e.g.*, for melting-point determinations, see p. 66).

4. Pour out the liquid as required, without letting the lip of the bottle touch the vessel into which you are pouring.

5. Touch any drop hanging from the lip of the bottle against the side of the stopper, and replace the latter in the bottle.

6. Replace the bottle in its proper place at once.

If it is necessary to place a stopper on the bench, make sure that it is not contaminated, and that two or more stoppers are not confused and replaced in the wrong bottles.

If a few drops of a liquid are required, it is advisable to pour a little of the liquid into a test-tube or watch-glass, and then transfer drops from this to the desired vessel with a dropping pipette or glass rod. Do *not* insert the pipette or rod into the reagent bottle.

Liquids frequently used are placed in wash-bottles (Fig. 4, 2). The liquid is expelled from the fine jet J by blowing down the tube T.

In most elementary classes, only one wash-bottle is provided; this should be used for distilled water. Liquids of which drops are frequently required (*e.g.*, indicators) may be stored in bottles fitted with dropping pipettes, or in medicine droppers.

TRANSFER WITH MEASUREMENT

Measured volumes of liquid may be transferred from one vessel to another by means of pipettes of various kinds (see pp. 58-62).

TRANSFER OF THE WHOLE OF A GIVEN VOLUME OF LIQUID

It is impossible to transfer the whole of a given volume of liquid from one vessel A to another B without washing (unless the liquid does not wet surfaces, *e.g.*, mercury).

FIG. 4, 2
Wash-Bottle

If vessel B has a narrow neck, a funnel is placed in it. The liquid is
. . . . lip of vessel A
. . . . outside of A.
. . . . washed out
six times with small volumes . . . . (usually water
in inorganic work) from a . . . . owed to
drain as thoroughly as poss . . . . A few
drops of the sixth washing are tested with an appropriate reagent to determine whether the original liquid or solute has been completely removed from A (*e.g.*, if sulphuric acid is being transferred from A to B, the washings are tested with barium nitrate solution). If the original liquid or solute has *not* been completely removed, washing is continued until this is the case. The glass rod and funnel (if used) are then washed several times with water, care being taken that all washings fall into vessel B.

the lower side-tube X into the annular space S between O and I, and out through the upper side-tube Y.

Liquids when heated without agitation are apt to become superheated, *i.e.*, the temperature may be raised above the boiling-point without boiling taking place. A superheated liquid is unstable and if it is shaken it starts to boil, often with great violence. This is called "bumping." A liquid may usually be prevented from superheating by the addition of a few small porous chips *before heating is started*. The tiny air bubbles in the pores serve as foci for bubbles of vapour when the liquid reaches its boiling-point, and ensure smooth boiling. Porous chips should therefore be added to all liquids to be refluxed.

4, 9   COOLING

Vessels *containing materials to be cooled should be treated as follows* [1] :

Required Temperature	Treatment
"Room temperature," *i.e.*, 10-20°.	Place under running cold water tap.
0°	Place in crushed ice and water or in refrigerator.
−20° to −10°	Place in a mixture of crushed ice and common salt (equal bulk of each).

PRODUCTION OF REDUCED PRESSURES

4, 10   THE WATER PUMP

It is often necessary to reduce the pressure in a vessel below atmospheric pressure (*e.g.*, for filtration, see pp. 34-35). The simplest pump used for this purpose is the water pump (Fig. 4, 5). Water from the tap W flows in a rapid stream through the fine jet J of the pump P. This water carries the air from the tube T with it by friction down the outlet tube O. The air pressure in T and in any piece of apparatus

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[1] All temperatures in this book are on the Centigrade scale.

" Lighting-back."

A Bunsen burner in which the gas is burning at the jet J is said to have " lit back." This is due to the supply of gas being insufficient to keep the flame from passing down the tube of the Bunsen. When a Bunsen "lights back," the gases are incompletely burnt and poisonous carbon monoxide escapes. A Bunsen which has " lit back " must be turned out *immediately*, the air and gas supplies readjusted, and the burner relit.
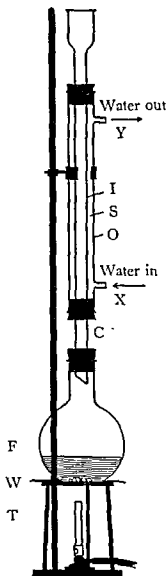
4, 7   WATER BATHS AND OIL BATHS

If it is necessary to heat a vessel to a constant temperature, or to heat a vessel containing inflammable liquids, the vessel should be placed in a bath of liquid (water for temperatures up to 100°, castor oil for temperatures up to about 250°), which is then heated by a Bunsen burner, by electricity or by steam. If the contents of the vessel are very inflammable (*e.g.*, ether, benzene, petroleum ether), and a Bunsen burner is the only available source of heat, a water bath is heated to the required temperature and the burner *turned out* before the vessel is introduced.

4, 8   REFLUXING

If a liquid has to be heated for a time to a temperature at or just below its boiling-point, and if the liquid is not to be evaporated, the vessel containing it must be provided with a reflux condenser, *i.e.*, a piece of apparatus which condenses the vapours and allows them to flow back into the vessel containing the hot liquid.

A simple reflux apparatus is illustrated in Fig. 4, 4. The flask F containing the liquid to be heated is supported on the wire-gauze W, and the tripod T. The condenser C consists of an inner tube I (within which the vapours rise and are condensed) and an outer tube O. I and O

FIG. 4, 4

Reflux Apparatus

may be fitted together with rubber stoppers as shown in the figure, or they may be fused together. A stream of water flows through

the lower side-tube X into the annular space S between O and I, and out through the upper side-tube Y.

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FIG. 4, 4

Reflux Apparatus

METHODS OF MIXING SUBSTANCES

4, II   LABORATORY METHODS

The mixing of substances is generally easy on the laboratory scale, although it may be very difficult on the factory scale. The importance to the chemist of mixing substances lies in the fact that molecules cannot interact unless they touch one another. Many pairs of substances mix spontaneously (*e.g.*, a pair of miscible liquids, a solid soluble in a liquid, any two gases). A pair of immiscible liquids may be brought into contact over a large surface by shaking or stirring them together. If contact is desired between a solid and a liquid in which it is insoluble, the solid should be finely powdered and shaken or stirred with the liquid. Another useful method is to treat the solid and liquid with a second liquid, in which both are soluble.

Satisfactory contact between two solids can be obtained only by melting them, or by treating a mixture of the solids with a liquid in which one or preferably both of the solids are soluble.

Layering.

Many tests, which depend on the production of colours when two liquids of different densities are mixed, are best observed by allowing the two liquids to diffuse slowly into one another. The process, known as layering, is carried out as follows. The more dense liquid is poured into a test-tube, which is then held in a slanting position while the less dense liquid is run down the side of the tube from a pipette so that it forms a separate layer on top of the denser liquid. If no colour appears as a result of diffusion at the interface, the liquids may be mixed slightly by holding the test-tube vertically between the palms of the hands, and rotating it gently by rubbing the palms together.

METHODS OF SEPARATING SUBSTANCES

Only those methods of separating substances which the student is likely to encounter in his practical work are described here. The simple operations—filtration and the separation of immiscible liquids—are dealt with first, followed by crystallisation and distillation, each of which involves several operations.

All the methods of separation discussed here depend on differences in physical properties between substances. In inorganic chemistry the materials present in a reaction mixture (products and unchanged starting materials) often show wide differences in physical properties and are therefore easy to separate. In organic chemistry the reverse is the case; where differences in physical properties between the constituents of a reaction mixture or of a natural product are slight, separation of the constituents is difficult and may involve many tedious

attached to the side-tube S is therefore reduced. A good water pump
reduces the pressure to about 10-15 mm. mercury (normal atmospheric
pressure is 760 mm. mercury). If, while the pump is connected to a
piece of apparatus, the pressure of water flowing through J decreases
on account of a change in pressure in the mains, or because someone
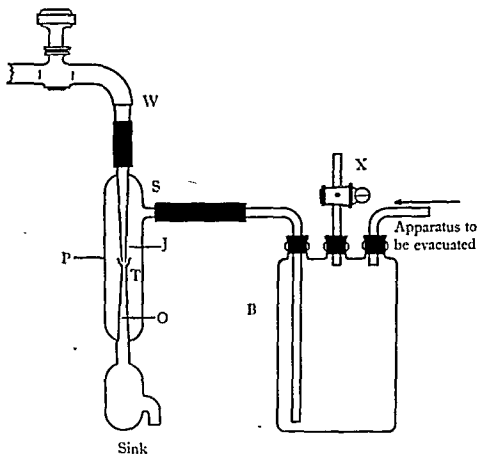
FIG. 4, 5

Water Pump and Trap

turns off the tap W by mistake, water is sucked back into the evacuated
apparatus and the experiment may be spoilt.

The safety-bottle B and tap X should therefore be introduced
between the pump and the apparatus to be evacuated. If any accident
occurs, water is sucked back into B, and does not reach the main
apparatus. If the bottle and tap are provided, the tap X should always
be opened to the air *before* the water tap is turned off.

If the bottle and tap are not provided, the evacuated apparatus
must be detached from S *before* the water tap is turned off.

perforated area of the plate but does not project up the sloping or vertical sides of the funnel. The paper is wetted with solvent and fitted tightly to the plate by gentle suction before the mixture to be filtered is poured on to it.

In one variety of suction filter (Fig. 4, 7, *C*) a perforated porcelain disc (Witt's plate, X) is fitted into an ordinary glass funnel F. A piece

C. Witt's Plate in Funnel

A. Büchner Funnel and Flask

B. Hirsch Funnel and Filter Tube
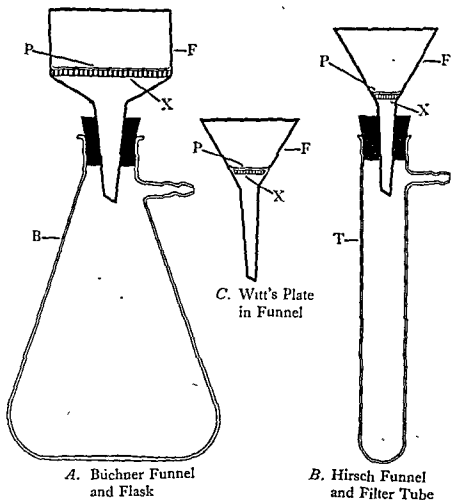
FIG. 4, 7
Suction Filters

of filter-paper P, slightly larger than the disc, is then placed on top of it and the filtration carried out as with the Büchner or Hirsch pattern funnels.

The advantages of Witt's plate are (1) that it is cheap ; (2) that it is easy to clean—there are no invisible parts as in the other porcelain filters. The disadvantage is that unless the plate and paper are fitted carefully into the funnel, solid will "leak" between the edge of the plate and the funnel.

repetitions of the processes outlined below (*e.g.*, crystallisation, distillation, extraction).

4, 12　　　　　　FILTRATION

A mixture of a solid and a liquid may be separated into its components by placing it on a filter, which allows the liquid but not the particles of solid to pass through. The filter is usually of paper, but may be of sintered glass, asbestos fibre or other finely divided solid. Most types of filter may be obtained in different degrees of porosity (*i.e.*, with different sizes of holes to retain solid particles of different sizes). Only paper filters are considered here.

THE SIMPLE FILTER

The simplest type of filter (Fig. 4, 6) is a paper P folded in quarters supported by a glass funnel F, the angle of which is approximately 60°.
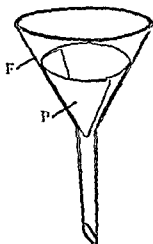
FIG. 4, 6
Simple Filter

Points to Note.

1. For rapid filtration the paper must fit the funnel closely. To ensure this, it may be necessary to make the second fold so that the paper is not folded exactly into quarters.

2. The paper should be wetted with the solvent to be used and pressed against the funnel over the whole surface, particular care being taken that it fits closely at the folds.

3. The top of the filter-paper should be about 1 cm. below the rim of the funnel.

4. The mixture to be filtered should be poured down a glass rod which nearly touches that part of the paper which is three folds thick.

5. The filter-paper should never be filled with liquid to within less than 0·5 cm. of the top edge.

THE SUCTION FILTER

The suction filter has two advantages over the simple filter, viz. (1) filtration is quicker; (2) the solid on the filter packs together bet . . . .
Th . . . .
P on the perforated plate X. The funnels are fitted with rubber stoppers into the necks of the receivers (B, Büchner flask; T, filter-tube), each of which has a side-tube for attachment to a water pump.

The paper must be of such a size that it covers the whole of the

portion of D, more A will pass into this. If the process is repeated sufficiently often, all the A will be contained in the D solutions, and all the B will remain in the C solution.

Suppose A=benzoic acid, B=glucose, C=water, D=ether. Benzoic acid is slightly soluble in water and very soluble in ether; glucose is very soluble in water and virtually insoluble in ether. A mixture of benzoic acid and glucose could therefore be separated into its constituents by dissolving the mixture in water and by extracting with ether. Benzoic acid passes into this solvent, while glucose remains in the water. The partition coefficient of benzoic acid between water and ether is 0·006. In other words, if an aqueous solution of benzoic acid is shaken with an equal volume of ether, 99·4% of the benzoic acid will pass into the ether.

The extractions are carried out in a separating funnel, the two liquids being shaken together to ensure contact and then allowed to stand until separation has taken place. The following points should be noted in addition to those mentioned on p. 36 :

1. When a volatile liquid (e.g., ether or chloroform) is being shaken in a separating funnel, the funnel should be inverted frequently and the pressure released by opening the tap for a moment.

2. Many pairs of liquids on vigorous shaking form emulsions which are difficult to separate. The vigour and duration of shaking should if possible be such that emulsions are not formed (see p. 49 regarding the use of the centrifuge in separating emulsions).

A quantitative experiment on partition coefficients is described on p. 159. The partition of a substance between two solvents can be shown very simply and strikingly as follows. Iodine is soluble in aqueous potassium iodide and in carbon tetrachloride, forming brown and violet solutions respectively. If a solution of iodine in aqueous potassium iodide is extracted with successive portions of carbon tetrachloride, the brown colour of the aqueous solution and the violet colours of successive extracts become steadily paler.

A solution containing 0·5 g. iodine and 1·0 g. potassium iodide per litre of water is provided. Take 20 ml. of this solution and extract it with three successive portions of carbon tetrachloride. Note the colours of the aqueous and carbon tetrachloride layers after each extraction.

4, 15

CRYSTALLISATION

The use of crystallisation as a method for purifying solids depends upon two principles. First, when a substance crystallises, the molecules arrange themselves in a regular pattern in space, called a lattice. Molecules of different kinds do not usually fit into the same lattice, and therefore crystallisation is as a rule synonymous with purification.

FILTRATION OF HOT MIXTURES

If a hot mixture has to be filtered through any type of apparatus, the latter must first be heated to the temperature of the mixture by pouring hot solvent through it [1] (see crystallisation, p. 40).

4, 13   THE SEPARATING FUNNEL

Two immiscible liquids which differ appreciably in density can be separated because one sinks below the other. The apparatus used to separate such liquids is the separating funnel (Fig. 4, 8).

The mixture of liquids to be separated is poured into the funnel and allowed to stand until the two liquids have separated. The denser liquid is then run off through the tap T. The less dense liquid may also be run off through T, or may be decanted through the opening at the top of the funnel.

Points to Note.

1. Do *not* grease the tap T ; in nearly every separation one of the two liquids will dissolve or react with the grease. T should be lubricated with a few drops of one of the liquids to be separated.

FIG. 4, 8
Separating
Funnel

2. Do *not* try to run liquid out of the tap T without removing the stopper S to admit air.

4, 14   EXTRACTION OF ONE LIQUID BY ANOTHER

Suppose a solution of two substances A and B in a solvent C is shaken with another solvent D, which is immiscible with C. Suppose A is soluble but B insoluble in D. Some A, but no B, will pass into solution in D. The substance A will distribute itself between the two liquids C and D in the ratio

$$\frac{\text{solubility of A in C}}{\text{solubility of A in D}}.$$

This ratio is called the *partition coefficient* of A between C and D. If C and D are separated in a funnel and C is shaken with a fresh

---

[1] In more advanced work, filters fitted with heated jackets may be available.

Crystallisation of the complex mixtures which may be obtained from natural products or from reactions is a difficult art. Repeated crystallisation or fractional crystallisation must frequently be carried out (for details see other books). The following method, however, illustrates the principles involved, and covers simple examples which the student is likely to meet.

GENERAL INSTRUCTIONS

The following symbols are used :

> X=substance to be crystallised.
>
> S=solvent.
>
> A=an impurity which is more soluble in S than is X.
>
> B=an impurity insoluble in S.

1. Choice of Solvent.

This is governed by the following requirements :

(a) S must not react with X.

(b) The difference between the solubilities of X in S at the latter's boiling-point and at room temperature should be as large as possible.

(c) Impurities should either be more soluble in S than is X, or insoluble in S.

(d) It is preferable that the boiling-point of S should be below the melting-point of X.

The most commonly used solvents are the following :

For inorganic compounds : water.

For organic compounds : water, methyl alcohol, ethyl alcohol, ether, acetone, acetic acid, ethyl acetate, petroleum ether (various fractions), benzene, toluene, chloroform, pyridine ; mixtures of these (e.g., water and ethyl alcohol, methyl alcohol and ether). Some general rules about the solubilities of organic compounds are given on p. 298.

If nothing is known about the solubilities of a substance which has to be crystallised, small-scale tests are carried out with likely solvents, using the solid ($\frac{1}{4}$ to $\frac{1}{2}$ spatula-point) and solvent (1 to 10 drops or more) in small tubes (2 in.×$\frac{1}{4}$ in.).

(There are some exceptions, *e.g.*, when two isomorphous substances form mixed crystals.) Secondly, if a solid A is soluble in a liquid B, the solubility of A in B is nearly always greater when hot than when cold. If therefore a hot saturated solution of A in B is cooled, the solution cannot contain all the A present, and some A separates in solid (probably crystalline) form.

The crystallisation of benzoic acid from water serves as an example. The variation with temperature of the solubility of benzoic acid in water is shown in Fig. 4, 9. Suppose 100 ml. of water at 90° are saturated with benzoic acid. The weight of acid (4·65 g.) dissolved

FIG. 4, 9

Solubility of Benzoic Acid in Water

is represented by AC. Suppose the solution is cooled to 20°. At this temperature the solubility of the acid is only 0·25 g. per 100 ml. (represented by BC). An amount of acid represented by AB (4·40 g.) separates as solid. The cold saturated solution of the acid from which this solid may be separated by filtration is called the *mother-liquor*.

Since crystallisation is usually synonymous with purification, if benzoic acid containing impurities which are more soluble in water (*e.g.*, urea) is crystallised from water, these impurities will probably remain in the mother-liquors and not contaminate the crystalline benzoic acid. Impurities which are insoluble in the solvent (*e.g.*, charcoal) may be removed by filtering the hot solution.

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2. Dissolving the Crude Solid.

When a promising solvent (S) has been found, the crude solid (X+A+B) is placed in a test-tube, boiling-tube or conical flask, a small volume of S is added, and the mixture heated and stirred. If S is water, the tube or flask may be heated by a Bunsen burner ; if S is any organic solvent, the tube or flask must be heated in a bath which has previously been heated to a temperature above the boiling-point of S and then removed from the flame. Further small volumes of S are added with constant stirring *either* until the solid is all dissolved (if no B is present) *or* until the bulk of solid does not decrease on heating and stirring for a minute (if B is present). If X tends to crystallise immediately the tube or flask is removed from the source of heat, about 10% more S is added to avoid crystallisation in the filter at the next stage.

Coloured or tarry impurities of high molecular weight may often be removed from the desired substance by preferential adsorption on finely-powdered charcoal. Charcoal (1-2 spatula-points per 10 ml. solvent) is added to the solution of the impure material, the mixture is refluxed for a few minutes and filtered hot.

3. Hot Filtration.

The hot solution must be filtered in all cases (even when no solid is visible in it), since most crude solids contain traces of dust or shreds of filter-paper. A simple filter with a *short stem* fitted with an ordinary paper is heated by pouring boiling pure S (10-20 ml. for a small crystal-lisation) through it. As soon as the pure S has passed through, a clean test-tube or flask is placed under the funnel and the hot solution prepared as described in the previous paragraph is poured on to the filter. S+X+A pass through the filter ; B remains on it.

4. Cooling the Filtrate.

The hot filtrate (S+X+A) is now cooled to obtain pure X. If the melting-point of X is below or about the same as the boiling-point of S, X may tend to separate as an oil. In this case the filtrate should be allowed to cool as slowly as possible. If the melting-point of X is well above the boiling-point of B, X will separate as a solid, and the filtrate should be cooled rapidly under the cold water tap. This produces a crop of small crystals, which are usually purer than the large crystals obtained if the filtrate is cooled slowly.

In all cases the mixture must be cooled to room temperature (15-20°) before the cold filtration is carried out. If this is not done, the yield of recrystallised material is lowered. Fig. 4, 9 illustrates what happens if the solution of benzoic acid in water, discussed on p. 38, is cooled to 40° instead of 20°. The weight of pure benzoic acid obtained is 4·10 g. (AB′) instead of 4·40 g. (AB), the difference (B′B, 0·30 g.) is wasted in the mother-liquors.

5. Cold Filtration.

When the mixture is cold it is filtered by suction. Any solid which adheres to the vessel in which the mixture was cooled is washed on to the filter with the mother-liquor (which is a cold saturated solution of the desired substance). The solid is sucked dry on the filter, washed twice with small volumes of pure solvent to free it from traces of mother-liquor, and again sucked dry.

6. Drying.

The crystallised product is best dried in a vacuum-desiccator (see p. 50). In elementary work it is usually sufficient to dry it by pressing repeatedly on filter-paper.

The processes may be represented by the following diagram:

CRUDE SOLID

X+A+B

(Desired substance and impurities—one more soluble and one insoluble)

Treat with hot solvent S; filter hot.

HOT FILTRATE

S+X+A

(Solvent, desired substance and more soluble impurity)

SOLID ON FILTER

B

(Insoluble impurity)

Cool; solid separates; filter cold.

COLD FILTRATE

S+A+some X

(Solvent, more soluble impurity, some of desired substance)

Mother-Liquor.

SOLID ON FILTER

X

(Desired substance, pure)

EXPERIMENTS

1. Recrystallisation of Benzoic Acid from Water.

X=benzoic acid ; S=water ; A=urea ; B=charcoal.

A sample of impure benzoic acid (about 0·2 g.) containing approximately 10% urea and 1% charcoal is provided. Determine the melting-point of this material. Recrystallise the material, using boiling water (about 10 ml.). The product should be pure benzoic acid (colour, pure white ; m.p., 122° ; weight, approx. 0·1 g.).

2. Recrystallisation of Anthracene from Ethyl Alcohol.

X=anthracene; S=ethyl alcohol; A=other hydrocarbons from coal tar; B=charcoal.

A crude sample of anthracene (0·1 g.), to which a trace of charcoal has been added, is provided. Determine the melting-point of this material and recrystallise it from ethyl alcohol (about 15 ml.). The product should be fairly pure anthracene (slightly yellow leaflets, m.p. 212-213°; weight, approx. 0·05 g.).

3. Other Examples.

The following are suitable for students' experiments. Determine the melting-point of the crude solid, recrystallise about 0·2 g.–0·5 g. of it and determine the melting-point of the purified material. In all cases students must discover for themselves the volume of solvent necessary; in those cases where no solvent is recommended, they must choose a suitable solvent as suggested on p. 39.

Solid	M.p. of pure substance	Solvent recommended for crystallisation
Acetamide $CH_3.CONH_2$	81°	Acetone.
Acetanilide $C_6H_5.NH.CO.CH_3$	114°	Water.
Acetoxime $(CH_3)_2C:NOH$	60°	Petroleum ether (b.p. 40°-60°).
Benzaldehyde phenylhydrazone $C_6H_5.NH.N:CH.C_6H_5$	158°	Ethyl alcohol +water.
Benzene-azo-β naphthol $C_6H_5.N:N.C_{10}H_6.OH$	131°	Ethyl alcohol.
m-Dinitrobenzene $C_6H_4.(NO_2)_2$	90°	Ethyl alcohol.
β-Naphthol $C_{10}H_7.OH$	122°	Water.
	130°	
	161°	
	148°	
	133°	
	70°	
	159°	

REPORTS

These may be arranged as follows:

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CRYSTALLISATION

Material to be crystallised. Acetanilide (crude), pale buff amorphous powder, 0·5 g.

Choice of solvent. Small-scale tests gave the following results[1]:

Water. Material v. sol. in hot, sl. sol. in cold ; therefore satisfactory.
Ethyl alcohol. Material v. sol. in cold ; therefore useless.
Chloroform. Ditto.
etc. etc.

Solvent chosen. Water.

Crystallisation.
The crude material was treated with boiling water (15 ml.). Traces remained undissolved. The hot solution was filtered and the filtrate on cooling deposited colourless leaflets. These were filtered by suction[2] and dried.

Product. Weight 0·35 g.; m.p. 111–113°.
(M.p. of acetanilide given in the literature is 114°.)

4, 16   DISTILLATION

·The separation of liquids by distillation depends on the fact that liquids differ in boiling point, *i.e.*, in the temperature at which their vapour pressure is equal to the atmospheric pressure.[3]
The apparatus used for distillation (see Fig. 4, 10, *A* for a simple example) consists essentially of four parts. These are :

1. A vessel for heating the liquid to be distilled (distilling flask, F).
2. A thermometer T, to register the temperature of the vapour which is distilling.
3. A condenser C, to transform vapour back into liquid.
4. A receiver R, to collect distillate.

Instructions for setting up the apparatus are given on pp. 46–47. The distilling flask is heated gradually (an oil bath or water bath, if available, should be used in preference to a naked flame), so that a liquid of lower boiling-point distils almost completely before a liquid of high boiling-point starts to distil. Each different liquid is collected in a separate receiver. The course of the distillation may be followed by plotting volume of liquid distilled against boiling-point. The graph for an *ideal* distillation of a mixture of chloroform and aniline is shown by the *dashed line* in Fig, 4, 11. Here the temperature registered by the thermometer rises abruptly from room temperature to the boiling-point of chloroform (61°) and remains constant at this point while all the chloroform distils ; it then rises abruptly to the boiling-point

distillation are not considered here.

2. Recrystallisation of Anthracene from Ethyl Alcohol.

X=anthracene ; S=ethyl alcohol ; A=other hydrocarbons from coal tar ; B=charcoal.

A crude sample of anthracene (0·1 g.), to which a trace of charcoal has been added, is provided. Determine the melting-point of this material and recrystallise it from ethyl alcohol (about 15 ml.). The product should be fairly pure anthracene (slightly yellow leaflets, m.p. 212-213°; weight, approx. 0·05 g.).

3. Other Examples.

The following are suitable for students' experiments. Determine the melting-point of the crude solid, recrystallise about 0·2 g.-0·5 g. of it and determine the melting-point of the purified material. In all cases students must discover for themselves the volume of solvent necessary ; in those cases where no solvent is recommended, they must choose a suitable solvent as suggested on p. 39.

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Benzaldehyde phenylhydrazone $C_6H_5.NH.N:CH.C_6H_5$.	158°	Ethyl alcohol +water.
Benzene-azo-β naphthol $C_6H_5.N:N.C_{10}H_6.OH$.	131°	Ethyl alcohol.
m-Dinitrobenzene $C_6H_4.(NO_2)_2$.	90°	Ethyl alcohol.
β-Naphthol $C_{10}H_7.OH$.	122°	Water.
Benzamide $C_6H_5.CONH_2$ . .	130°	
	161°	
	148°	
	133°	
	70°	
	159°	

REPORTS

These may be arranged as follows:

10 Oct. 1945.

CRYSTALLISATION

Material to be crystallised. Acetanilide (crude), pale buff amorphous powder, 0·5 g.

of aniline (184°), remains constant at this point while the aniline
distils, and finally falls abruptly to room temperature when all the
liquid in the distilling flask has been volatilised.
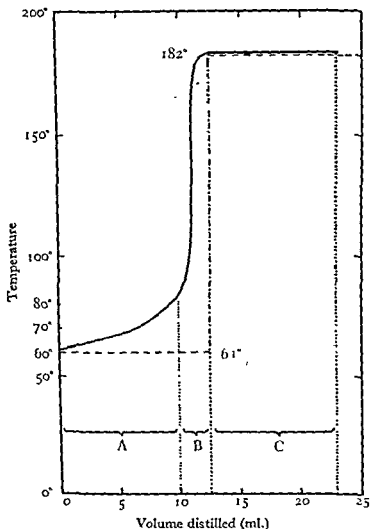
FIG. 4, 11

Distillation Curves

Distillation of a mixture of chloroform and aniline (equal volumes)

- - - - - - -   Ideal curve
—————   Actual curve

In practice the graph is similar in shape to this, but the corners are
" rounded off " (*e.g.*, *full line* in Fig. 4, 11, which shows the graph
for an *actual* distillation of chloroform and aniline). The reasons for
the " rounding off " of the corners are as follows : (1) The elevation

B. Using Conical Flask and Adapter

A. Using Distilling Flask

Water in

Water out

Fig. 4.10
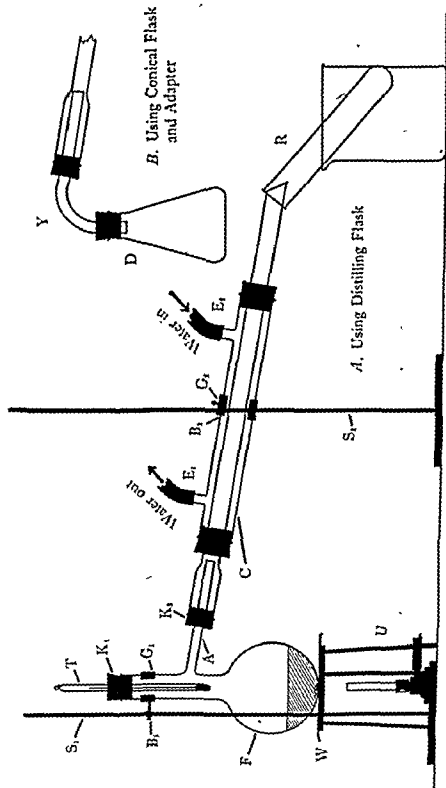
Distillation Apparatus

Fit the flask F carrying its two corks K_1 and K_2 and the thermometer T into G_1 so that the latter holds the neck of the flask gently but firmly, and the flask just rests on the centre of the wire gauze.[1]

Fit two pieces of rubber tubing E_1 and E_2 for outlet and inlet of water to the side-tubes of the condenser C.

Place the stand S_2 with its boss-head B_2 and clamp G_2 as shown in Fig. 4, 12, A (*not* as in Fig. 4, 12, B) in such a position that the

A The Right Way   B The Wrong Way
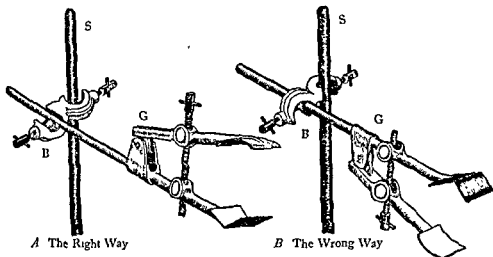
FIG. 4, 12

Fitting of Boss-Heads and Clamps

clamp will hold the condenser C at the correct angle just opposite the end of the side-arm A. When the position of C is correct, tighten up the screws of boss-head B_2 firmly, loosen clamp G_2, slide the condenser up [2] and press it firmly but gently on to the cork K_2. Tighten up the clamp G_2 gently. Place the receiver R in position, supporting it on a beaker or blocks of wood.

3. Distillation.

Remove the cork carrying the thermometer, put into the flask two or three porous chips to prevent bumping (see p. 31), then insert a funnel, the stem of which passes below the side-arm, and pour in the liquid to be distilled. (A suitable mixture is one of chloroform and aniline (equal volumes).) This should fill *not more than half* the bulb of the flask. Replace the cork and thermometer.[3] Turn on the water for the condenser.

[1] The arrangement shown in Fig. 4, 10, B is convenient when a liquid has

of the boiling-point of chloroform by the aniline present.[1] (2) The time
taken for the ⸻ ⸻ come into equilibrium with the vapour
round it. (3) ⸻ ⸻ apparatus the separation
into chloroform and ⸻ ⸻ the temperature
range 84°-182° a mixture of chloroform ⸻ distils. By slow
heating in a bath these imperfections can be minimised.

Pairs of liquids, the boiling-points of which differ by 50° or more,
may be separated fairly well by the simple apparatus illustrated and
described here. For liquids between whose boiling-points the differ-
ence is less than 50°, a more elaborate apparatus including a fraction-
ating column is necessary.

PRACTICAL DETAILS

1. Boring and Fitting of Corks.

Choose a sound cork of such diameter that it slips into the neck of
the flask up to about a third of its length. Soften it by means of a
cork-crusher or by wrapping it in paper and rolling it gently under foot.
Choose a *sharp* cork-borer of diameter equal to or slightly less than
that of the thermometer. Bore a hole through the centre of the cork ;
go half-way through from one end, then remove the borer and bore
from the other end, so that the two holes meet in the middle of the
cork. This method of boring ensures that the ends of the hole are
clean-cut. Do *not* force the borer hard ; rotate it to and fro with
gentle pressure. Bore a cork similarly to connect the side-arm of the
distilling flask with the condenser. If the holes in the corks are not
quite wide enough for the objects which have to be inserted, widen
them by very *gentle* filing with a circular file (rat's-tail file).

Lubricate the hole in the thermometer-cork with a drop of glycerol,
and insert the thermometer with very gentle pressure and rotation.
Hold the thermometer near the point where you are pressing it into
the cork, *not* at the top. (If you hold it near the top and force it hard,
you will probably break it and cut your hand.)

To insert the cork into the neck of the flask, grasp the neck of the
flask firmly at the top, and press in the cork carrying the thermometer
gently and firmly with a rotatory movement. (Do *not* hold the flask
by the bulb and force the cork in hard. If you do, you will probably
break the flask and cut your hand.)

2. Assembly of Apparatus.

Place the stand S_1, tripod U and wire gauze W in the positions shown
in Fig. 4, 10, A. Fit the boss-head B_1 and clamp G_1 to the stand ;
the shaft of the clamp should rest in the boss-head as shown in
Fig. 4, 12, A. (Contrast Fig. 4, 12, B ; here, as soon as the screw is
loosened, the clamp falls out of the boss-head.)

---

[1] The chloroform fraction A, as shown on the graph, distilled at 61°-84°.
When this fraction was redistilled alone, it all boiled at 61°-62°.

4, 17   THE CENTRIFUGE

The centrifuge (Fig. 4, 13) is a means of increasing artificially the force of gravity. It is used to separate a liquid and a solid, or two immiscible liquids of different density, when the force of gravity alone is insufficient. It is particularly valuable for separating fine powders and emulsions which are slow to separate. Most modern centrifuges are electrically-driven. Those used in the laboratory or in the side-room in clinical work have capacities from 50 ml. to 1 litre, and run at speeds up to 4000 revolutions per minute.

Containers are used in pairs, and the members of each pair (vessels and contents) must be carefully balanced against one another and
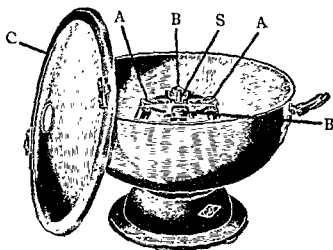
FIG. 4, 13
Centrifuge

placed in opposite buckets (AA or BB) of the centrifuge. With small tubes (10-15 ml.) it is sufficient to compare by eye the volumes of the liquids in the two tubes. If the tubes are not balanced a very severe stress is placed on the vertical shaft S of the centrifuge. The cover C is placed on the centrifuge, which is then started at its minimum speed. The speed is increased slowly by means of a resistance, but the *maximum speeds* laid down by the manufacturers *must not be exceeded.* After the required time, the centrifuge is allowed to slow down gradually. The worker should not try to interfere with its slowing down, because this is dangerous, and because fine precipitates may be jerked into suspension again if the speed is decreased too abruptly. If a solid has been separated from a liquid, the liquid is sucked off by means of a pipette or decanted carefully. If two liquids have been separated, one or both of them are sucked off by means of a pipette or water pump.

Heat the flask with a small non-luminous flame. Chloroform starts to distil soon ; the temperature shown by the thermometer rises quickly to approximately 61°[1] and then gradually to about 80°. Heat very gently until the distillation slackens, then increase the size of the flame. When the thermometer reaches 85° remove the first receiver R₁, which now contains pure chloroform[2] (fraction A in Fig. 4, 11), and substitute receiver R₂. Heat the flask slowly until the thermometer registers 120°. At this point turn off the water supply to the condenser, and drain the latter. Continue heating until the temperature reaches about 180° and distillation becomes rapid again. Replace receiver R₂ (containing chloroform-aniline mixture ; fraction B in Fig. 4, 11) by receiver R₃. The temperature will now remain fairly constant at some temperature between 180° and 185° until the flask is almost dry. The fraction distilling at this temperature is pure aniline (fraction C in Fig. 4, 11).

Measure the volumes of the three fractions with your measuring cylinder, and place them in the stock-bottles for recovery.

4. Reports.

These may be arranged as shown in the following example. A sketch of the apparatus, with parts labelled, should be included for the first distillation only. Notes on manipulation (*e.g.*, on crushing and boring of corks) are not required.

10 Oct. 1945.

DISTILLATION

Material distilled. Mixture of equal volumes of chloroform and aniline (25 ml.). Dark brown liquid.

Apparatus and method. As in Klyne, *Practical Chemistry*, pp. 43-48.

Fractions collected.

No.	Boiling range	Volume (ml.)	Appearance and smell
1	61°–84°	10·0	Colourless ; smell of chloroform.
2	85°–182°	2·0	Very pale yellow, smell of aniline.
3	184°–186°	10·5	

Residue in flask. Very small volume, almost black liquid.

---

[1] This initial temperature may not be exactly 61° because most students' thermometers may be up to 2°-3° in error, and because the atmospheric pressure may differ appreciably from 760 mm.

[2] This fraction may be slightly cloudy due to the presence of traces of water, which distil with the chloroform.

BERNHAUER, K. Einführung in die organisch-chemische Laboratoriumstechnik. Springer, Berlin, 1934.
(A most systematic survey of organic practical methods. Provides good practice in translating simple chemical German.)

GATTERMANN, L. Laboratory Methods of Organic Chemistry. (Translated from the 22nd German edition by MCCARTNEY, W.) Macmillan, London, 1934.

REILLY, J., and RAE, W. N. Physico-Chemical Methods, 4th edition, 2 vols. Methuen, London, 1943.
(Advanced.)

WILSON, C. L. An Introduction to Microchemical Methods. Methuen, London, 1938.

Also the books listed at the end of the next chapter (p. 71) which are mainly concerned with measurement.

4, 18   DRYING OF SOLIDS AND LIQUIDS

The removal of *water* from solids and liquids is of such importance, especially in organic chemistry, that a special section is given to it, although the principles involved are the same as those involved in other separations.

SOLIDS

Solids may be dried by pressing on filter-paper or on porous tile. They may be dried more efficiently if they are placed in a vacuum desiccator (Fig. 4, 14) together with a substance that absorbs water (anhydrous calcium chloride or phosphorus pentoxide), and the desiccator evacuated. The desiccator consists of a body B and a lid L, fitted together by a ground-glass joint, which is greased. The drying agent is placed in the base of the desiccator (at D) and the substance to be dried is placed in an open vessel on the porcelain plate P. The tap T is opened, and the side-tube A attached to the water pump; the desiccator is evacuated and T is closed. When air is admitted to the evacuated desiccator, T must be opened slowly, otherwise the sudden inrush of air will probably blow the dried material all over the inside of the desiccator.

FIG. 4, 14
Vacuum Desiccator

LIQUIDS

Liquids are usually dried by the addition of a substance which absorbs water (anhydrous calcium chloride or sodium sulphate; sodium metal; phosphorus pentoxide). A drying agent must be chosen which does not interact with the substance from which water is to be removed. After a suitable time the liquid is decanted or filtered from the solid.

Substances which are hygroscopic or which react readily with moisture may be prevented from absorbing moisture from the air by keeping them in a desiccator or in sealed vessels.

FURTHER READING

ROBERTSON, G. R. Laboratory Practice of Organic Chemistry, Revised edition. Macmillan, New York, 1943.
(Includes a good short treatment of the theoretical principles on which practical methods—*e.g.*, distillation, crystallisation—are based.)

in outline move when the beam is raised by turning the knob A.
The parts are as follows:

Z   base.

YY   supports for pans.

X   central pillar.

A   knob for raising beam.

N   vertical arrestment rod which when A is turned raises the
agate plate L_3. This in turn raises the knife-edge K_3,
attached to the beam B and the two knife-edges K_1 K_2.

L_1 L_2 stirrups, provided with agate plates, raised by the knife-edges
K_1 K_2, and raising in turn the pans P_1 P_2.

O   object to be weighed.

W   weights.

R   rider.

H   carrier for rider.

The pointer Q and the scale S are shown only in Fig. 5, 1.
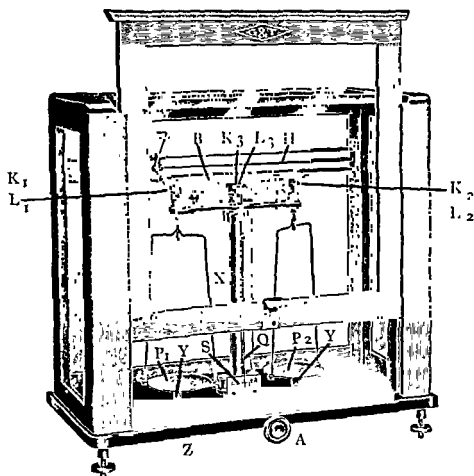
FIG. 5, 1
Balance

MEASUREMENT

This chapter should be used in conjunction with that on General Ideas on Quantitative Work (pp. 13-22).

MEASUREMENT OF MASS

5, 1   THE BALANCE

The *mass* of a body is a measure of the amount of matter in it. The *weight* of the body is the force with which this mass is attracted by the earth. When the chemist says that the weight of a sample is 2·3 grams he really means that the mass is 2·3 grams, but the habit of referring to this as a weight is of too long standing to be altered now.

The balance is an instrument for comparing the mass of any object with standard masses called " weights." The balance consists of a lever (the beam) supported by a central fulcrum (knife-edge). The pans on which objects are placed are hung from knife-edges at the ends of the beam. All but the crudest balances are provided with some means of supporting the beam and pans, so that the knife-edges do not have to carry their weight except when the balance is in use. The simplest kind of balance works on the same principle as a grocer's scales. The object to be weighed is placed on one pan, and weights are added to the other pan until the beam is horizontal, and the pointer attached to it is vertical.

Successive refinements are as follows. First, instead of waiting for the beam to become stationary, weights are added until the beam oscillates so that the pointer swings evenly on either side of a zero mark. Secondly, weights less than 10 mg. are too small to handle conveniently. Accurate balances are therefore provided with a *rider* which is a single movable weight that may be placed on the beam at different distances from the fulcrum, and may thus be equivalent to different weights placed on the pan.

Thirdly, in the most accurate type of weighing, the object is *nearly* counterpoised by the mass of the weights and the rider. The swings of the pointer are then measured, and used to determine the difference between the mass of the object and the mass of the weights+rider. Few elementary laboratories are likely to have balances with which it is profitable to try weighing by swings. For details if required see Vogel, *Quantitative Inorganic Analysis*, Longmans, Green, 1944, pp. 204-205.

A balance suitable for students' use (sensitive to $\frac{1}{2}$ mg.) is illustrated in Fig. 5, 1 and its essential parts are sketched in Fig. 5, 2 (p. 54). The parts shaded in Fig. 5, 2 are fixed to the base ; the parts shown

tative instruments, should be calibrated. No details are given here, since few elementary classes have the time for calibrating weights.

Beams calibrated for three types of rider are illustrated in Fig. 5, 4. In each case the unloaded balance is in equilibrium when the rider is on the zero mark. When using a beam of type A the student is recommended to move the rider only along the right-hand half of the beam; if the left-hand half is used the weight represented by the rider must be *subtracted* from the weights on the pan. When using a beam of the type C only the left-hand half of the beam should be used; confusion may arise if the right-hand half of the beam, which represents weights between 10 mg. and 20 mg., is used.
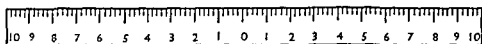
A. 10 mg. Rider. Zero-mark over Fulcrum
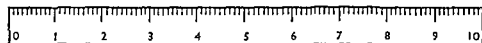
B. 5 mg. Rider. Zero-mark over Left-Hand Pan
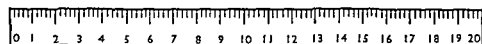
C. 10 mg. Rider. Zero-mark over Left-Hand Pan

Fig. 5, 4

Balance Beams

(Calibrated for different types of rider)

Instructions for the Use of the Balance

1. Release the beam and see whether the pointer swings freely and symmetrically about the zero point. If it does, the balance may be used; if it does not, ask a demonstrator to adjust the balance for you. If the beam does not oscillate when released, it may be set in motion by "fanning" air on to one of the pans with your hand.

2. Place the material to be weighed in a vessel of some kind (*e.g.*, weighing bottle, beaker, watch-glass); never place materials directly on the pan. Allow objects to come to the temperature of the balance before weighing them.

3. Never add weights or other objects to the balance pans or remove them from the pans while the beam is swinging.

4. Wipe the object to be weighed with a clean cloth or chamois

A set of weights is illustrated in Fig. 5, 3. Weights of 1 g. and upwards are usually cylindrical and made of brass or stainless steel; they are marked with the weight in grams. Smaller weights are usually
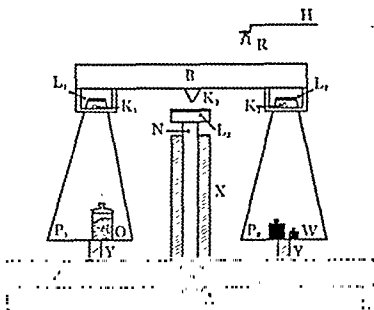
FIG. 5, 2
Balance
(Essential Parts)
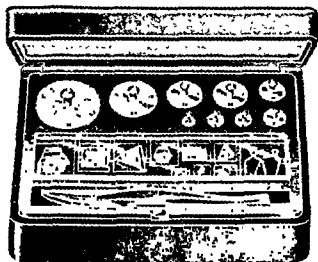
FIG. 5, 3
Weights

leaf-shaped and made of aluminium, nickel-silver or stainless steel; they are marked with the weight either in grams, thus, *e.g.,* " 0·5 g.", or in milligrams, thus, *e.g.,* " 500 mg." Weights, like all other quanti-

READING OF LEVELS

A good light is essential. If in difficulty the worker should stand with his back to the light and hold a piece of white paper behind the vessel which he is reading, or use a burette reader (Fig. 5, 8). For water and for all other liquids which form a meniscus which is concave, the *bottom* of the meniscus (P in Fig. 5, 5 *A*) is read. For mercury, which forms a convex meniscus, the *top* of the meniscus is read (Q in

A.	*B.*	*C.*
Water Meniscus	Mercury Meniscus	Parallax Errors
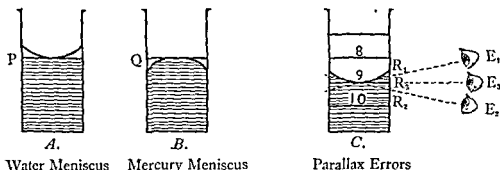
FIG. 5, 5

Reading of Levels

Fig. 5, 5, *B*). To avoid parallax errors the eye must be on the same level as the part of the meniscus read. These errors are illustrated in Fig. 5, 5, *C*. The eye at E_1 is too high, and the reading R_1 is too low (8·7 ml.). The eye at E_2 is too low, and the reading R_2 is too high (9·3 ml.). The eye at E_3 is in the correct place, and the reading R_3 is correct (9·0 ml.).

VESSELS GRADUATED " TO CONTAIN "

Some vessels (*e.g.*, graduated flasks, certain types of pipettes) are graduated *to contain* a stated volume of liquid in given conditions. Most liquids, except mercury, wet surfaces with which they are in contact, and when they are run out of a vessel a film of the liquid is left on the surface. If, therefore, vessels of this type are used to transfer the stated volume of liquid from one vessel to another, they must be thoroughly rinsed out after they have drained.

VESSELS GRADUATED " TO DELIVER "

Other vessels (*e.g.*, burettes, transfer pipettes) are graduated *to deliver* a stated volume or volumes of liquid in given conditions. With such vessels, consistent results can be obtained only if the conditions of drainage are consistent. Attention must be paid to (1) the cleanliness of the surface, (2) the time of drainage, (3) the position in which the vessel is held, (4) the contact of the delivery jet with solid or liquid surfaces.

leather and place it on the left-hand pan. Place a weight presumed to be larger than the weight of the object on the right-hand pan with forceps and release the beam. Then use the other weights in the box systematically to determine the weight of the object to the nearest 10 mg. below it. Close the front of the balance case, which has been open up to this point.

5. With the beam arrested, place the rider on the 5 mg. mark, release the beam, and note whether this weight is greater or less than that of the object. Adjust the rider until the pointer swings evenly on either side of the zero mark. It will be found with most student balances that adjustments of less than 0·5 mg. with the rider make no appreciable difference to the swings. Results should therefore be stated in the form: *e.g.*, 4·2175 g. or 3·3290 g.—it being realised that the fourth place of decimals is correct only to the nearest 5 units.

6. When equilibrium has been attained, add up the weights on the pan, add the weight represented by the rider and note the total in your note-book at once. Check the weights as you return them to the box.

7. Do not leave weights or other objects on the balance pans.

8. If material has to be added to or taken from vessels (*e.g.*, weighing bottles) remove them from the balance case.

9. Leave the balance clean and close the case.

MEASUREMENT OF VOLUMES OF LIQUIDS

5, 2   GENERAL

Units

The unit generally employed in scientific work for measuring volumes of liquids is the *millilitre* (ml.). This is the one-thousandth part of a litre, which is the volume occupied by one kilogram of water at 4° C. The millilitre is for all practical purposes identical with the older unit, the *cubic centimetre* (c.c.): 1·000000 ml.= 1·000027 c.c.

Temperature

The volume of a liquid and the volume of the vessel containing it are affected by temperature. Volumetric apparatus is usually calibrated for a temperature of 20° C. which is taken as normal laboratory temperature. The error introduced by changes of temperature between 15° C. and 25° C. is 1 in 1000 or less. This is less than the random variation for most volumetric work and may therefore be disregarded here. The variation with temperature in the volumes of liquids must, however, be borne in mind as a possible source of error in more accurate work.

The only pipettes likely to be met in an elementary chemistry course are the common transfer pipette and the graduated pipette.
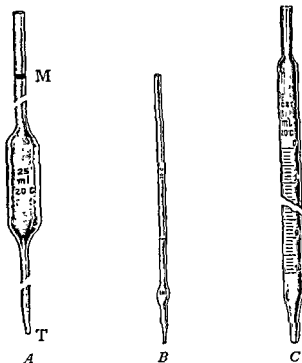
FIG. 5, 6

Pipettes

A Common Transfer   *B* Ostwald   *C* Graduated

THE COMMON TRANSFER PIPETTE

Purpose. To deliver a stated volume of liquid.

Sizes available. 1 ml. to 100 ml. For class use generally 10 ml. or 25 ml. (Fig. 5, 6, *A*).

Method of Use.

If wet with any liquid other than the one to be transferred, the pipette is washed out three times with small volumes of the latter. The liquid to be transferred is then sucked up in the pipette to a point just above the graduation and. M

is wiped dry with filter-paper, and the liquid is allowed to run out until the bottom of the meniscus is in the plane of the graduation-mark. The tip T is touched against the surface of the liquid in use, so as to remove any drop hanging from the tip. The pipette is then moved to the vessel into which the liquid is to be transferred and allowed to discharge its contents, being held vertically with its tip touching the

ACCURACY. CALIBRATION

The accuracy of all quantitative apparatus should be ensured by buying guaranteed apparatus or by calibration before use. The principles of calibration have been dealt with on p. 21, and detailed instructions for the calibration of a transfer pipette are given on pp. 60-61. Instructions for the calibration of other volumetric apparatus should be obtained from other books.

The labour of calibration can be saved by buying apparatus which has been calibrated by the National Physical Laboratory (NPL) or which is guaranteed by the manufacturers to conform with NPL standards.

The NPL has two classes for apparatus, viz., " Class A " for best work, and " Class B " for ordinary work. Some manufacturers provide apparatus which they guarantee to be within " Class B " limits at prices little more than those charged for ordinary apparatus.

Details of NPL standards for transfer pipettes are given on p. 60. For standards for other instruments see the NPL pamphlet, *Tests on Volumetric Glass-ware*.

PRECISION

The volumes of liquid contained in or delivered by the same piece of volumetric apparatus in successive operations show random variations like all other quantitative data.

In titrations in which volumes of 10 ml. or more are used, these variations are relatively small if the apparatus is clean and is carefully and consistently handled. They may, therefore, be neglected in comparison with other random variations involved in a titration, the biggest among which is that caused by the size of the drop used to produce the end-point colour change. (Figures for the random variations obtained with 10 ml. transfer pipettes are given on p. 60.) However, in titrations in which the volumes used are approximately 1 ml. or 0·1 ml., the random variations are considerable even with the most careful manipulation. Conway, *Micro-Diffusion Analysis and Volumetric Error* (Crosby Lockwood, 1939), deals with these variations very thoroughly.

5, 3   PIPETTES

Pipettes may be divided into three main classes:

1. Those calibrated to deliver a single stated volume (*e.g.*, the common transfer pipette, Fig. 5, 6, *A*; some Ostwald pipettes, Fig. 5, 6, *B*).

2. Those calibrated to contain a single stated volume (*e.g.*, some Ostwald pipettes, Fig. 5, 6, *B*, some blood pipettes).

3. Those calibrated to deliver any volume up to a stated maximum (the graduated pipette, Fig. 5, 6, *C*).

by the volume of 1·000 g. water at the temperature of the balance-room is the mean volume which would be delivered by the pipette at 20°.

Temperature	Volume of 1·000 g. water (ml.)
10°	1·002
15°	1·002
20°	1·003
25°	1·004

OTHER PIPETTES

The Graduated Pipette.

Purpose. To deliver any volume of liquid up to a stated maximum.

Sizes available. 1 ml. (graduated in 0·01 ml.) to 25 ml. (graduated in 0·1 ml.). 10 ml. (graduated in 0·1 ml.) is convenient for class work (Fig. 5, 6, C).

Method of use. These pipettes are used in the same way as transfer pipettes; they are not as accurate as the latter.

The Ostwald Pipette.

Purpose. To deliver or contain a stated volume of liquid.

Sizes available. 0·1 ml. to 10 ml. (Fig. 5, 6, B).

Method of Use.

(a) When calibrated to deliver a stated volume, these pipettes are used in the same way as the ordinary transfer pipette.

(b) If the pipette is calibrated to contain a stated volume, liquid is sucked up until the bottom of the meniscus is on the mark; it must *not* be sucked above the mark and then allowed to run down to this. The pipette is then allowed to deliver in the usual way, but no time need be allowed for drainage as the liquid remaining in it is rinsed out by washing two or three times with an appropriate liquid (for all aqueous solutions use water).

The Simple Tube Pipette.

This pipette is highly recommended by Conway (*op. cit.*, p. 26) for volumes of 1–2 ml. It is made by drawing hard glass tubing out to a capillary tip and calibrating with water.

Blood Pipettes.

These are of many different types; some are calibrated to contain, others to deliver the stated volumes; some are made to permit the dilution of blood with an aqueous solution in a known ratio. For

side of the vessel throughout the period of discharge. The inside of
the vessel, where it is in contact with the tip of the pipette, should be
slightly inclined to the vertical. After the meniscus has come to rest
at the bottom of the pipette, the pipette is left in the same position
to drain ... ... The drop
... ... of shaken out.

The above is based on the conditions of test used by the National
Physical Laboratory, since all reliable apparatus made in this country
is calibrated by NPL methods. Slightly different methods are recom-
mended by other authorities, but the differences are of no importance
for elementary work. The student must, however, realise that unless
a pipette is handled in precisely the same way as it was handled when
calibrated, it will not deliver the volume stated on it.

Accuracy.

NPL tolerances for some pipettes are as follows :

Capacity of Pipette (ml.)	10	25
Tolerance, Class " A ", ml.	±0·02	±0·03
Tolerance, Class " B ", ml.	±0·04	±0·06

This means that the average delivery of a Class " B " 10 ml. pipette
at 20° will be somewhere between 9·96 ml. and 10·04 ml.

Precision.

The random variations in pipette delivery are usually so small
that they may be neglected in comparison with other random variations
in titration. Conway (*Micro-Diffusion Analysis and Volumetric Error*)
gives the following ranges for Class " A " pipettes :

          10 ml. pipette ; range=mean ±0·012 ml.
          25 ml. pipette ; range=mean ±0·020 ml.

The chief source of random variation in pipette delivery is variation
in the amount of fluid left behind on the walls after the nominal
delivery. For this reason the reproducibility and constancy
of drainage is most important.

Calibration.

These instructions are for a 10 ml. or 25 ml. pipette. The pipette
is cleaned with chromic acid and thoroughly washed with water as
described on p. 25. Five successive pipette-fulls of distilled water
are then weighed (to the nearest 10 mg.) in a weighed stoppered
flask, the pipette being handled as described above. The *mean of
the five weights* [1] of water is calculated ; this mean weight, multiplied

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[1] The *range* of the five observations, i.e., the difference between the smallest
and the greatest, should not exceed 0·04 g. for a 10 ml. pipette or 0·06 g. for a
25 ml. pipette. If it does, the pipette is not being handled with sufficient care
and further practice in its use is necessary.

by the volume of 1·000 g. water at the temperature of the balance-room is the mean volume which would be delivered by the pipette at 20°.

Temperature	Volume of 1·000 g. water (ml.)
10°	1·002
15°	1·002
20°	1·003
25°	1·004

OTHER PIPETTES

The Graduated Pipette.

Purpose. To deliver any volume of liquid up to a stated maximum.

Sizes available. 1 ml. (graduated in 0·01 ml.) to 25 ml. (graduated in 0·1 ml.). 10 ml. (graduated in 0·1 ml.) is convenient for class work (Fig. 5, 6, C).

Method of use. These pipettes are used in the same way as transfer pipettes; they are not as accurate as the latter.

The Ostwald Pipette.

Purpose. To deliver or contain a stated volume of liquid.

Sizes available. 0·1 ml. to 10 ml. (Fig. 5, 6, B).

Method of Use.

(a) When calibrated to deliver a stated volume, these pipettes are used in the same way as the ordinary transfer pipette.

(b) If the pipette is calibrated to contain a stated volume, liquid is sucked up until the bottom of the meniscus is on the mark; it must *not* be sucked above the mark and then allowed to run down to this. The pipette is then allowed to deliver in the usual way, but no time need be allowed for drainage as the liquid remaining in it is rinsed out by washing two or three times with an appropriate liquid (for all aqueous solutions use water).

The Simple Tube Pipette.

This pipette is highly recommended by Conway (*op. cit.*, p. 26) for volumes of 1-2 ml. It is made by drawing hard glass tubing out to a capillary tip and calibrating with water.

Blood Pipettes.

These are of many different types; some are calibrated to contain, others to deliver the stated volumes; some are made to permit the dilution of blood with an aqueous solution in a known ratio. For

side of the vessel throughout the period of discharge. The inside of the vessel, where it is in contact with the tip of the pipette, should be slightly inclined to the vertical. After the meniscus has come to rest at the bottom of the pipette, the pipette is held in the same position to drain for 15 seconds and is then removed from the vessel. The drop remaining in the tip is *not* blown or shaken out.

The above is based on the conditions of test used by the National Physical Laboratory, since all reliable apparatus made in this country is calibrated by NPL methods. Slightly different methods are recommended by other authorities, but the differences are of no importance for elementary work. The student must, however, realise that unless a pipette is handled in precisely the same way as it was handled when calibrated, it will not deliver the volume stated on it.

Accuracy.

NPL tolerances for some pipettes are as follows :

Capacity of Pipette (mL.)	10	25
Tolerance, Class " A ", ml.	±0·02	±0·03
Tolerance, Class " B ", ml.	±0·04	±0·06

This means that the average delivery of a Class " B " 10 ml. pipette at 20° will be somewhere between 9·96 ml. and 10·04 ml.

Precision.

The random variations in the volumes of liquid obtained by successive deliveries from the same pipette, if carefully handled, are so small that they may be neglected in comparison with other random variations in titration. Conway (*Micro-Diffusion Analysis and Volumetric Error*) gives the following ranges for Class " A " pipettes :

> 10 ml. pipette ; range=mean ±0·012 ml.
> 25 ml. pipette ; range=mean ±0·020 ml.

The chief source of random variation in pipette delivery is variation in the amount of fluid left behind on the walls of the pipette after delivery. For this reason close attention to cleanliness and to methods of drainage is necessary.

Calibration.

These instructions are for a 10 ml. or 25 ml. pipette. The pipette is cleaned with chromic acid and thoroughly washed with water as described on p. 25. Five successive pipette-fulls of distilled water are then weighed (to the nearest 10 mg.) in a weighed stoppered flask, the pipette being handled as described above. The *mean* of the five weights [1] of water is calculated ; this mean weight, multiplied

Method of use.

The tap T of the burette must be properly greased to prevent leakage. Remove the tap. Dry it and its socket with a clean duster, smear a very little vaseline evenly over the surface of the tap and re-insert it in the socket. Turn the tap to and fro until an even film of vaseline covers its whole surface. (When this is the case, the surface between tap and socket is invisible.)

If the burette is wet with any liquid other than the one to be used, it is washed out three times with the latter, care being taken to see that the whole of the internal surfaces *above and below the tap* T are wetted at each washing. If any particles of excess vaseline from the tap have been dislodged, remove these so that they cannot clog the jet during the titration. The burette is then filled above the zero-mark and the liquid run out until the bottom of the meniscus is on the zero-mark. (The space S below the tap must *not* contain an air bubble, and there must *not* be a drop hanging from the jet J.) To define the meniscus sharply, a burette reader (Fig. 5, 8; a half-white, half-black visiting card with two incisions) is slipped over the burette and adjusted so that the top of the black part is just below the bottom of the meniscus. The eye must be on a level with the meniscus to minimise parallax errors. When liquid has been run out of the burette, any drop hanging from the jet J is removed by touching the side of the receiving vessel against J. The level of the liquid is then read as before to the nearest half-graduation (*i.e.*, 0·05 ml.).

OTHER BURETTES

The Pinchcock Burette.

Burettes similar to those described above, but with a pinchcock on a piece of rubber tubing instead of a glass-tap, are sometimes used for the sake of economy. These are less satisfactory than the glass-tap burettes for most purposes, since it is impossible to be sure that there is no air bubble in the rubber tube, and since solutions may react with the rubber. The pinchcock burette is advantageous for some special purposes. (For an example, with illustration, see p. 390).

The Micro-Burette.

For the measurement of volumes of 1–2 ml. with an accuracy of 0·01 ml., burettes similar to those described above are available. These usually have a reservoir attached, from which the burette may be refilled as necessary.

The Conway Burette.

For the delivery of volumes of about 0·1 ml. with an accuracy of 0·001 ml., the horizontal tube burette designed by Conway (*op. cit.*, p. 38) may be used.

details see Hutchison and Hunter, *Clinical Methods*, 11th edition, Cassell, 1941 ; or *Notes on Clinical Laboratory Methods*, University of Glasgow, 5th edition, 1944.

MEASUREMENT OF POISONOUS AND VOLATILE LIQUIDS

If a poisonous but non-volatile liquid has to be measured it may be sucked into a pipette by attaching a length of rubber-tubing and sucking with the mouth[1] or with the water-pump, and pinching the rubber tubing when the liquid has been sucked above the mark.

Very volatile liquids (*e.g.*, ether) cannot satisfactorily be measured with a pipette ; they should be measured from a burette.

5, 4   **BURETTES**

THE COMMON BURETTE

Purpose. To deliver any volume of liquid up to a stated maximum.

Sizes available. 10 ml., 25 ml., 30 ml., 50 ml. (graduated in 0·1 ml.) (Fig. 5, 7).
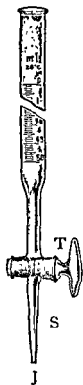
FIG. 5, 7
Common Burette
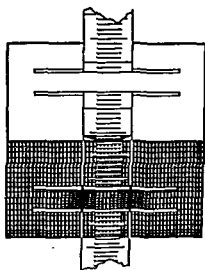
FIG. 5, 8
Burette Reader

[1] This method is used in bacteriological work ; a cotton-wool filter is included to prevent organisms being sucked into the mouth.

Method of use.

The tap T of the burette must be properly greased to prevent leakage. Remove the tap. Dry it and its socket with a clean duster, smear a very little vaseline evenly over the surface of the tap and re-insert it in the socket. Turn the tap to and fro until an even film of vaseline covers its whole surface. (When this is the case, the surface between tap and socket is invisible.)

If the burette is wet with any liquid other than the one to be used, it is washed out three times with the latter, care being taken to see that the whole of the internal surfaces *above and below the tap* T are wetted at each washing. If any particles of excess vaseline from the tap have been dislodged, remove these so that they cannot clog the jet during the titration. The burette is then filled above the zero-mark and the liquid run out until the bottom of the meniscus is on the zero-mark. (The space S below the tap must *not* contain an air bubble, and there must *not* be a drop hanging from the jet J.) To define the meniscus sharply, a burette reader (Fig. 5, 8; a half-white, half-black visiting card with two incisions) is slipped over the burette and adjusted so that the top of the black part is just below the bottom of the meniscus. The eye must be on a level with the meniscus to minimise parallax errors. When liquid has been run out of the burette, any drop hanging from the jet J is removed by touching the side of the receiving vessel against J. The level of the liquid is then read as before to the nearest half-graduation (*i.e.*, 0·05 ml.).

OTHER BURETTES

The Pinchcock Burette.

Burettes similar to those described above, but with a pinchcock on a piece of rubber tubing instead of a glass-tap, are sometimes used for the sake of economy. These are less satisfactory than the glass-tap burettes for most purposes, since it is impossible to be sure that there is no air bubble in the rubber tube, and since solutions may react with the rubber. The pinchcock burette is advantageous for some special purposes. (For an example, with illustration, see p. 390).

The Micro-Burette.

For the measurement of volumes of 1-2 ml. with an accuracy of 0·01 ml., burettes similar to those described above are available. These usually have a reservoir attached, from which the burette may be refilled as necessary.

The Conway Burette.

For the delivery of volumes of about 0·1 ml. with an accuracy of 0·001 ml., the horizontal tube burette designed by Conway (*op. cit.*, p. 38) may be used.

5, 5   THE GRADUATED FLASK

Purpose. To contain a stated volume of liquid.

Sizes available. 10, 25, 50, 100, 250, 500, 1000 ml. 250 or 500 ml. flasks are convenient for class use (Fig. 5, 9).

Method of use.

Fill at the correct temperature with liquid until the bottom of the meniscus is on the graduation-mark. See that the liquid is roughly homogeneous before finally adjusting to the mark. After adjusting to the mark *shake thoroughly* to ensure that the liquid is completely homogeneous.
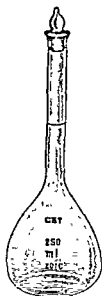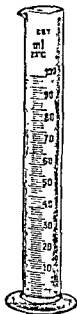
FIG. 5, 9   FIG. 5, 10
Graduated Flask   Measuring Cylinder

5, 6   THE MEASURING CYLINDER

Purpose. To deliver any volume of liquid up to a stated maximum.

Sizes available. 10, 25, 50, 100, 250 ml. (graduated in $\frac{1}{10}$ ml.) to 1 l. (graduated in or 100 ml. (graduated in 1 ml.) 5, 10).

Use.

Measuring cylinders are used only for *approximate* measurements. They are often calibrated at the top graduation-mark only, and the remaining marks made on the assumption that the vessel is of even diameter throughout. Since this is sometimes far from true, a 25 ml. measuring cylinder should *not* be used for measuring 2 ml. of liquid.

MEASUREMENT OF TEMPERATURE

5, 7
THE THERMOMETER

Method of Use

The bulb must be placed at the point, the temperature of which it is required to measure, and time must be allowed for the thermometer to come into equilibrium with its surroundings.[1] (These two points may seem very obvious, but students often place the bulb of the thermometer in wrong positions.) In many cases (*e.g.*, in a distillation) only the bulb and a small part of the stem of the thermometer are at the temperature which is to be measured, and a large part of the stem is at a lower temperature. The reading of the thermometer is therefore lower than it should be. In advanced work a correction known as the emergent stem correction must be made to rectify this.

Calibration

This may be carried out in one of two ways:

1. The temperature of a bath of liquid is measured simultaneously with the thermometer to be calibrated and with a standard thermometer. The bath is successively heated to 20°, 30°, 40°, etc. and a table of corrections made.

2. When a thermometer is kept for a particular purpose, *e.g.*, the determination of melting-points, it is convenient to calibrate it by measuring with it the properties (melting-point, boiling-point, etc.) of pure substances, for which these properties have already been determined accurately with standard apparatus.

5, 8
DETERMINATION OF MELTING-POINTS

The melting-point is of exceptional importance in testing the purity and identity of organic compounds. The principles involved and the information that may be gained from melting-points are discussed in Chapter 6 (pp. 119-120).

Apparatus

The simplest types of apparatus for melting-point determination are shown in Fig.   bath of liquid (flask F or

a sample of the substance, the   mined. The bath is heated by

The two types of apparatus differ only in the method by which the bath liquid is circulated. The flask type depends on convection, the beaker type has a stirrer S, which is moved up and down by hand.

The tube used for the sample (melting-point tube) is shown (full-size) at Fig. 5, 11, C.

[1] These notes deal only with mercury-in-glass thermometers.

E

Dibutyl phthalate, $C_6H_4(COOC_4H_9)_2$, is recommended as a bath liquid since it is an inert liquid of high boiling-point which may be heated repeatedly to 250° without discoloration. Concentrated sulphuric acid, which is often used, is dangerous.
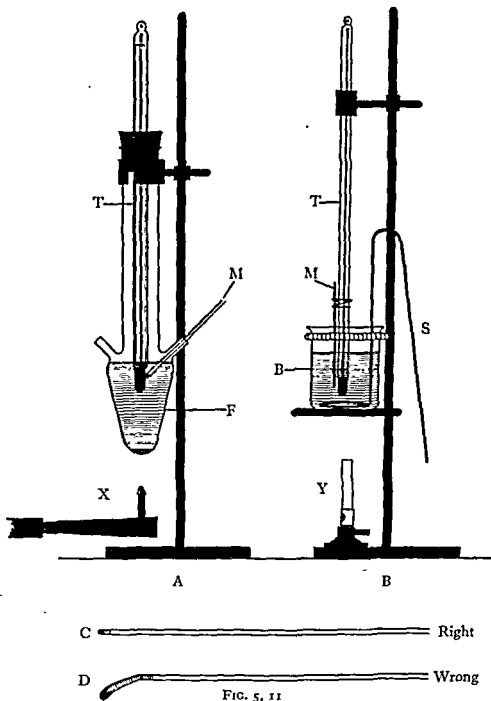
FIG. 5, 11

A and B. Melting-point Apparatus
C and D. Melting-point Tubes

METHOD

1. Preparation of Tube.

The tubes are made by heating clean soft-glass tubing in a blowpipe flame until it softens, then drawing it out to a diameter of 1 mm. and cutting the tubing into pieces about 70 mm. long.[1] One end of the tube is se
rotating it.
Fig. 5, 11, C)
is the result of plunging the tube into the middle of the flame.)

2. Drying and Powdering of Sample.

The sample must be dry and finely powdered. If it has been dried beforehand, a few mg. (a bulk about that of 20 particles of table salt) are finely powdered on a watch-glass with a spatula. If the sample has not been dried beforehand, it may be dried and powdered simultaneously by pressing a spatula-point of the solid repeatedly on a piece of porous tile about 1 in. square, until it appears to be dry. When doing a mixed melting-point each sample should be dried separately; approximately equal quantities of the samples are then mixed on a watch-glass and powdered finely.

3. Filling of Tube.

The mouth of the melting-point tube is pressed into the sample, and a quantity of the latter sufficient to form a layer about 1 mm. deep in the tube is introduced.[2] The material is driven to the bottom of the tube by tapping the latter on the bench.

4. Determination.

The tube is then placed beside the thermometer as shown in Fig. 5, 11, A or B. With the flask apparatus, the tube is slipped into one of the side tubes; with the beaker apparatus the tube is pressed against the side of the thermometer, to which it adheres on account of the surface-tension of the bath liquid. If there is no information about the probable melting-point of the substance, a rough determination of this is carried out first, the bath being heated rapidly until the substance melts; an accurate determination is then carried out on another sample as described below. If the melting-point of the substance is known approximately, the bath is heated rapidly to a temperature 20° below this before the substance is introduced. The rate of heating is then reduced to 3°-5° per minute, and the sample and the thermo-

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[1] The author considers it economical to provide students with these tubes ready made.
[2] The correct amount is shown in Fig. 5, 11, C. The tube in Fig. 5, 11, D contains far too much solid.

meter watched until the sample has completely melted. The following data should be recorded [1]:

1. Temperature at beginning and end of melting.
2. Temperature at which softening (if any) took place before melting.
3. Occurrence of browning or frothing (if any); these usually indicate decomposition.

In a simple case where no preliminary softening, no browning and no frothing take place, the results may be stated thus: *e.g.*, "m.p. 122°-123°." In a case where all these complications enter, the results may be stated thus, *e.g.*:

> "Substance softened 204°, browned slightly 210°, melted with more browning and frothing 214°-216°."

5, 9   DETERMINATION OF BOILING-POINTS

The boiling-point is of great value for the identification of pure substances. The influence of impurities on boiling-points is complicated and will not be considered here. Unlike the melting-point, the boiling-point cannot be used in any simple way as a criterion of purity. The boiling-point of a pure liquid may be determined by the distillation apparatus described on pp. 43-47 or by a similar smaller apparatus. If only 1-2 ml. of liquid are available the determination may be carried out as follows. The liquid is placed in a filter-tube, fitted with a cork carrying a thermometer, the bulb of which is about half an inch above the surface of the liquid. The tube is clamped vertically, and to the side-arm is attached a piece of rubber tubing long enough to hang over the edge of the bench, so that inflammable vapours will not be ignited. The liquid is heated with a very small flame until it boils (a blowpipe flame as illustrated in Fig. 5, 11, A is convenient). The steady temperature reached by the thermometer, when its bulb is surrounded by vapour, is the boiling-point of the liquid.

MEASUREMENT OF COLOUR

5, 10   COMPARISON OF COLOUR TINTS

The student is introduced at the beginning of any chemistry course to the use of colour tests. In their simplest form these tests offer no difficulties, *e.g.*, if a liquid turns blue litmus red, it is acid; if a solution gives a red colour with potassium thiocyanate solution, it contains ferric iron.

Acid-base indicators are considered in elementary work simply as distinguishing between "acid" and "alkaline" solutions; they can,

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[1] In advanced work it is necessary to state whether the melting-points are "corrected" (for emergent stem) or "uncorrected."

however, as explained in Chapter 6, be used to measure the acidity or *p*H of a solution with some accuracy if fine graduations of colour are noted. For this purpose it is necessary to *compare* the colour obtained on adding the indicator to the sample of *unknown p*H value with those obtained by adding the indicator to a series of samples of *known p*H values. If the unknown sample is colourless, the comparison can be made satisfactorily by viewing unknown and standard samples in test-tubes of the same kind against a white background in daylight (natural or artificial). For examples see the experiments on hydrogen-ion concentration (pp. 163-167).

If, however, the unknown sample is itself coloured (*e.g.*, urine), it is not sufficient merely to add indicator to it and to the standards, and then compare the colours so obtained. To make a fair comparison the colours of the standards must be blended with the colour of the sample. This is done by means of a comparator (Fig. 5, 12), a box with sheets of ground-glass GG on two sides, and with spaces for 6 test-tubes (1-6).

Source of light

Eye
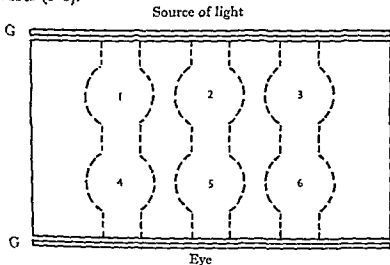
FIG. 5, 12

Comparator

Three tubes of the unknown sample are placed in spaces 1, 2, 3. Tubes of different standards (*e.g.*, buffers of *p*H 7·0 and 8·0) are placed in spaces 4 and 6. A tube of water is placed in space 5. Indicator (the same number of drops in each tube) is then added to tubes 2, 4, and 6, and the colours are compared by viewing towards the light as shown. If the colour of $(2+5)$ is intermediate in tone between those of $(1+4)$ and $(3+6)$, the *p*H of the unknown sample is between 7·0 and 8·0; the comparison is then repeated using standards of *p*H 7·0 and 7·5 or 7·5 and 8·0.

A test-tube rack with two parallel rows of holes will serve as a makeshift comparator. It is improved by placing pieces of white card between adjacent pairs of holes.

5, 11   MEASUREMENT OF COLOUR INTENSITY

The concentrations of many substances in solution may be determined by measuring the intensity of colour either of the substances themselves or (more often) of substances produced by reactions between them and other materials. Such methods of analysis, which are called colorimetric, are widely used in biochemistry, since they are quick and often applicable to very dilute solutions.

All colorimetric methods depend in principle on the comparison of the intensities of colour of the sample of unknown concentration and of samples of known concentrations. Only the simplest method, the *standard series method*, is described here. For details of more complicated methods, *e.g.*, those involving the use of plunger-type colorimeters, step photometers, or photoelectric colorimeters, see other books. The standard series method consists in comparing directly with the naked eye the colour intensities of the unknown sample and of a series of known samples. The samples (equal volumes) are placed in flat-bottomed glass tubes and the colours viewed by placing the tubes side by side on a white paper or tile and looking down through them vertically.

The concentration of the unknown is the same as that of the known sample which gives the same colour intensity. For accurate work specially prepared tubes made of colourless glass with uniform bore, called Nessler tubes, are used. For class work flat-bottomed sample tubes (3 in.× 1 in.) with a 20 ml. graduation-mark are satisfactory.

Example.—Nessler's determination of ammonia.

When an alkaline solution of potassium mercuri-iodide (K_2HgI_4) is added to a solution of an ammonium salt a brown colour is produced.[1]

A standard solution of ammonium chloride containing 0·010 mg. NH_3 per ml. is provided. Into six graduated sample tubes take respectively 0·0, 1·0, 2·0, 3·0, 4·0, 5·0 ml. of the standard solution, dilute each to 20 ml. with the ammonia-free water provided, add to each Nessler's reagent (1·0 ml.) and mix by gentle shaking. These standards[2] contain 0, 0·010, 0·020, 0·030, 0·040, 0·050 mg. NH_3.

Take 10 ml. of the given unknown ammonia solution in a graduated sample tube, dilute to 20 ml. with ammonia-free water, add Nessler's reagent (1·0 ml.) and mix by gentle shaking. Allow the tubes to stand for 10 minutes, and then compare the colour of the unknown with those of the known samples by looking down through the tubes vertically on to a white paper or tile. Draw your conclusions, and calculate the concentration of the unknown solution in mg. NH_3 per litre.

In more accurate work, if the colour given by the unknown

[1] A precipitate is formed by high concentrations of ammonium salts.
[2] Ready-made standards may be provided to save time.

... . and 0·030 mg.

.... .2, 0·024, 0·026,

.... .. .ate of the concentration of the unknown made by comparison with these.

If the colour obtained with the unknown sample shows that this is more concentrated than the most concentrated standard sample, the unknown must be diluted in a known ratio, so as to obtain a solution which is within the range of the standards.

A colorimetric method often used in clinical work is the determination of haemoglobin by the haemoglobinometer. In Sahli's method a known volume of blood is added to a known volume of 0·1N-HCl and diluted with water until the colour of the mixture matches that of a single arbitrary standard.

FURTHER READING

VOGEL, A. I. A Text-Book of Quantitative Inorganic Analysis. Longmans, Green, London, 1944.

TREADWELL, F. P. Analytical Chemistry, Vol. II, Quantitative Analysis (Translated by HALL, W. T.), 8th edition. Wiley, New York, 1935.

CONWAY, E. J. Micro-Diffusion Analysis and Volumetric Error. Crosby Lockwood, London, 1939.
(This book deals very thoroughly with volumetric error, and with a special method of titration using volumes of about 0·1 ml.)

REILLY, J., and RAE, W. N. Physico-Chemical Methods, 2 vols., 4th edition. Methuen, London, 1943.

NATIONAL PHYSICAL LABORATORY. Tests on Volumetric Glass-ware. Tests on Balances, Weights and Densities. Tests on Thermometry. National Physical Laboratory, Teddington, Middlesex.

GENERAL AND PHYSICAL CHEMISTRY

CHAPTER 6

PRINCIPLES AND THEIR APPLICATIONS

6, 1   INTRODUCTION

The purpose of this chapter is to outline those physico-chemical principles, an understanding of which will be of value to the student in his later work, and which can be illustrated in an elementary course. Chief among these principles are the Kinetic Theory, the Law of Mass Action, the Ionic Theory and certain ideas on Molecular Structure. The word " understanding " in the first sentence must be emphasised. By " understanding " is meant a grasp of the ideas such that the student can apply them to his own problems in subsequent work. A mere parrot-like learning, however accurate, is of little value.

It is assumed that the student has a thorough understanding of the Atomic Theory and of the Laws of Proportion, which are the basis of quantitative work. These cannot be dealt with in this book, except in so far as the Law of Constant Proportions is illustrated by volumetric analysis. It is also assumed that the student has an elementary knowledge of the nature of acids, bases and salts, and is familiar with the fact that most reactions of salts are (in terms of the older theories) reactions characteristic of the acidic or the basic radical.

According to the Kinetic Theory molecules are considered as being in constant motion. The theory provides, as will be shown below, useful if crude molecular pictures of the gaseous, liquid and solid states, and of physical and chemical changes taking place in and between these states. The Law of Mass Action deals with the relation between the concentrations of substances and the rate of chemical action between them. The idea of dynamic equilibrium as a balance between two opposing processes is of great importance because many processes occurring in living organisms are balance actions.

The Ionic Theory deals with the nature of electrolytes (acids, bases and salts) in aqueous solution. Since nearly all living organisms either live in an aqueous medium or carry their own aqueous medium round with them in the form of a blood system, and since this aqueous medium (external or internal) and the living cell itself contain many

electrolytes, the importance of the Ionic Theory in biological science cannot be overstated.

All but certain special types of cells live very close to " neutrality." Small alterations in acidity or alkalinity—so small as to be of little account in most purely chemical work—are incompatible with life ; phenomena caused by very small alterations in acidity must therefore be considered in detail.

No detailed account of molecular structure can be given here. The structures of the most important types of compounds will be briefly considered in the light of modern ideas on the structure of the atom, valency and the Periodic Classification.

Parts of this chapter (pp. 88-91 and 100-117) deal with the application of the theoretical ideas mentioned above to analytical methods. The value of analysis to the medical student is not that it teaches him how to identify or determine a particular substance, but that, in addition to illustrating general scientific principles discussed in Part I, it illustrates in many simple ways the Law of Mass Action and the Ionic Theory, which have a wide application in his future work.

Other aspects of physical chemistry—oxidation and reduction, osmotic pressure, colloidal solutions—which are of great biological importance, are considered in the later sections of this chapter.

PRINCIPLES

6, 2   THE KINETIC THEORY

Chemical and physical changes in and between the three states of matter may conveniently be visualised in terms of the kinetic theory as follows.[1]

In a gas, the molecules move about freely in a space very much larger than their own volume. They therefore travel relatively long distances between collisions. (An analogy from everyday life is provided by a number of people in a park. Everyone can meet everyone else, but may have to go a long way to do so.) In a liquid the molecules move about freely, but are packed tightly together. Except at the surface, each molecule is completely surrounded by others. (An analogy is provided by people in a crowded shop. They are free to move about, but anyone can move only by elbowing someone else out of the way.) In a solid the molecules do not move freely, they merely vibrate about certain positions which are fixed relatively to one another. (An analogy is provided by a body of men drilling. The body of men may be moved as a whole, and the individual men may

[1] The treatment of the kinetic theory given here is extremely crude ; fuller
  . . .   ls from his experience in
                                                  s the student to visualise

move their arms and legs, but they may not wander about and change places as in the previous analogies.)

The rate of any chemical or physical change depends on two factors: first, the number of molecules which *have a chance* to undergo the change and, secondly, the proportion of these molecules which actually *do* undergo the change in unit time.

The changes which can be considered in this way include many physical processes—*e.g.*, the boiling of a liquid, the solution of a solid in a liquid, the partition of a solute between two liquids, the phenomena taking place at a semi-permeable membrane—and all chemical reactions.

One most important conception which enters into the consideration of many changes is that of *dynamic equilibrium, i.e.*, a state in which two opposing processes go on at equal rates, so that no progress is made in either direction. One physical example is considered in a very rough way in the following paragraphs and a chemical example is considered on p. 76.

Consider a solid A placed in contact with a liquid (*e.g.*, water) in which it is soluble. Suppose that at any moment the number of A molecules which are exposed on the surface of the solid is x and that the concentration of A molecules in solution is [A]. In such a system two processes are constantly going on, viz.:

1. A molecules at the surface of the solid dissolve in the water.
2. Dissolved A molecules come out of solution and adhere to the surface of the solid.

The rate r_1 of the first process depends upon the number of A molecules which have a chance of dissolving (x) and on the proportion of these which do dissolve in each second (this proportion may be represented by a constant k_1) :

$$r_1 = k_1.x.$$

The rate r_2 of the second process depends upon x, the number of places to which dissolved molecules may adhere, [A] the concentration of dissolved molecules and k_2 a constant (which depends on the speeds of the dissolved A molecules and on the chance that a molecule which strikes the solid surface will adhere to it) :

$$r_2 = k_2.x. [A].$$

At equilibrium, *i.e.*, when the solution is saturated, $r_1 = r_2$,

$$k_1.x = k_2.x. [A]$$

$$[A] = \frac{k_1}{k_2} = \text{a constant.}$$

This constant is the *solubility* of A in water.

The above example brings out the importance of *surfaces* in any

process in which immiscible or partially-miscible materials are concerned. It is obvious, but none the less it is very often forgotten, that only molecules at the surface have a chance to take part in such a process. Furthermore, the molecules at the surface form only a very small proportion of the total number of molecules in the liquids or solids concerned. Contact may be improved by increasing the surface, but infinitely better contact and therefore better chance of interaction can be obtained if the two substances are dissolved in another liquid. Methods for the hydrolysis of fats illustrate these principles. Fats are virtually insoluble in water and in aqueous solutions. Hydrolysis by alkali or by enzyme in aqueous solution is therefore slow. The hydrolysis may, however, be accelerated (1) by the emulsification of the fat—by bile salts in the duodenum—providing a greater surface area for enzyme action, (2) by the use of a solvent in which both fat and alkali are soluble, viz., ethyl alcohol.

6, 3   THE LAW OF MASS ACTION

The Law of Mass Action states that the rate of any chemical reaction is proportional to the concentrations [1] of the reacting substances. Thus for the reaction

$$A + B = AB$$
$$\text{rate of reaction} = k.[A].[B] \qquad . \qquad . \qquad . \qquad (1)$$
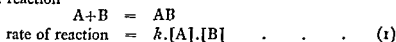
where k is a constant and $[A]$ and $[B]$ are concentrations in g. mols. per litre.[2]

Considered in terms of the kinetic theory, the rate of a reaction depends on (i) the number of collisions taking place between A and B molecules (i.e., the number of molecules which get a chance to react), (ii) the proportion of such collisions which result in the formation of AB molecules.

Factor (i) depends on the speeds and the concentrations of the molecules. At constant temperature the average speeds of the molecules are constant. Factor (ii) depends on the natures of A, B and AB and cannot be considered further here. At constant temperature, the proportion of collisions resulting in combination is constant. Thus at constant temperature the number of collisions between A and B molecules which result in combination, i.e., the rate of the reaction, depends solely on the concentrations of A and B molecules.

An experiment illustrating the variation in the speed of a reaction with the concentrations of reacting substances is described on pp. 159-160.

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[1] The expression " active mass " is more correct, but in elementary work the active mass may be taken as equal to the concentration.

[2] A formula within heavy square brackets represents a concentration in gram-molecules per litre; this is called the molar concentration or molarity of a solution, and is indicated by the letter M. Thus "0·123M-HCl" means a solution containing 0·123 g. mols. HCl per litre.

6, 4 REVERSIBLE REACTIONS. DYNAMIC EQUILIBRIUM

For the reversible reaction,

$$A + B \; \rightleftharpoons \; C + D,$$
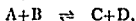
expressions for the rates of the forward and reverse reactions can be written as follows :

Rate of reaction between A and B, $r_1 = k_1.[A].[B].$

Rate of reaction between C and D, $r_2 = k_2.[C].[D].$

At equilibrium these two rates must be equal.

$$k_1.[A].[B] = k_2[C].[D] \qquad . \qquad . \qquad (2)$$

The ratio between the concentrations of the reacting substances at equilibrium is given by

$$\frac{[C].[D]}{[A].[B]} = \frac{k_1}{k_2} = K \qquad . \qquad . \qquad (3)$$

K is called the *equilibrium constant* of the reaction.

An equilibrium of this kind, which is called a *dynamic equilibrium*, is not a state in which nothing is happening, but a state in which *two opposing processes* are going on at *equal rates*. Unless this is understood it is difficult to see why changes should take place when the equilibrium conditions are disturbed.

A dynamic equilibrium may be upset by the *addition* of one of the reactants (A or B) or products (C and D), which causes an increase in the rate of the forward or reverse reaction respectively, and a displacement of the equilibrium in such a way as to use up the added material. The equilibrium may also be upset by the *removal* of one of the reactants or products, which causes a decrease in the rate of the forward or reverse reaction and a displacement of the equilibrium in such a way as to replace the material removed. Many examples of the disturbance of equilibria are discussed later.

Experiments illustrating the effects of disturbing an equilibrium mixture are described on pp. 160-162.

6, 5   THE IONIC THEORY

All electrolytes in aqueous solution are, to a greater or lesser extent, dissociated into positive ions (cations) and negative ions (anions). They may be divided into two classes, viz., *strong electrolytes* (most salts, some acids and bases), which are 100% dissociated, and *weak electrolytes* (other acids and bases), which are partly dissociated, thus, *e.g.*:

Strong Electrolyte $CuSO_4 \; \rightarrow \; Cu^{++} + SO_4^{--}$.

Weak Electrolyte $NH_4OH \; \rightleftharpoons \; NH_4^+ + OH^-$.
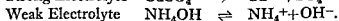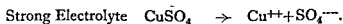
Full evidence for this will be found in theoretical text-books, but two pieces of evidence which are of great importance in connection with analysis are (i) the fact that certain reactions are common to all salts derived from the same acid while other reactions are common to all salts derived from the same base, and (ii) the almost instantaneous nature of reactions between electrolytes in solution. If, for example, a solution of barium nitrate is added to a solution of copper sulphate, a white precipitate of barium sulphate is formed. The same precipitate is obtained from a solution of *any* sulphate and a solution of *any* barium salt, and in all cases the precipitate is formed immediately. An experiment illustrating these principles is described on p. 162.

The identification of a simple electrolyte therefore falls into two quite distinct parts, viz., identification of the cation and identification of the anion. Furthermore, most methods of quantitative analysis applied to electrolytes are methods for the determination of an ion, and not for the determination of a substance.

It should be noted that the above-mentioned facts about reactions between electrolytes had led chemists, long before the Ionic Theory was suggested, to think of every salt as composed of two or more independent parts, viz., one or more acidic radicals and one or more basic radicals. Thus copper sulphate was considered as composed of the basic radical (Cu) and the acidic radical (SO_4). The method of cation identification used to-day (the Group Separation, see pp. 90-91 and 286-287) is essentially the same as that devised by Liebig in 1831.

6, 6   MOLECULAR STRUCTURE

THE PERIODIC CLASSIFICATION

The Periodic Classification, shown in a modified form in the Table on p. 79, groups the elements according to their chemical and physical properties into nine Groups (O-VIII), most of which may be subdivided into two Subgroups each, A and B. (For an account of the history of the Periodic Classification see theoretical text-books.)

In the Table the elements of the first two short periods in each Group are placed above the Subgroup whose members most resemble them.

ATOMIC STRUCTURE

The atom of an element is now thought to consist of a positively-charged *nucleus* .... ass of the atom; and a numbe .... rticles, the *electrons*, arrang .... The number of unit positive charges on the nucleus, which is equal to the number of electrons in the neutral atom, is called the *atomic number* of the element. The chemical properties of an atom depend largely on the number of electrons in the outermost shell. Chemical combination generally takes place in such a way that each atom obtains a *stable group* (most

frequently of 8 electrons in its outermost shell (see below). If two elements have the same numbers of electrons in their outermost shells, they show, in general, similar chemical properties. Modern physical evidence regarding electronic structures supports thoroughly the Periodic Classification, originally put forward on chemical evidence long before anything was known about the structure of the atom.

CHEMICAL BONDS

Purely chemical studies in the nineteenth century gave some evidence regarding the ways in which atoms are bound together in molecules by valency bonds. The valency of an element was one of the chief criteria for determining its place in the Periodic Table. So far as elementary organic chemistry is concerned, the valency ideas of the nineteenth century are largely adequate to-day. In inorganic chemistry, however, the picture has changed greatly.

There are two chief types of chemical linkage, viz., the *electrovalent linkage* and the *covalent linkage*.

In an *electrovalent linkage*, an *electron* is *transferred* from an atom B to another atom A. . B thus becomes a positive ion B^+, and A a negative ion A^-. The process may be represented as follows, the electrons in the outermost shell (valency electrons) being shown by dots :

$$B \cdot + \cdot \overset{..}{\underset{..}{A}} : \ = \ B^+ \ \ : \overset{..}{\underset{..}{A}} : ^-$$

An electrovalent linkage is *always ionic* in solution, in the liquid, and

reactive metals have one, two or three electrons only in their outermost shells and tend to lose these. The atoms of the more reactive non-metals have one, two or three electrons less than a stable group of eight in their outermost shells, and

a group of eight. Thus, for follows :

$$Na \cdot + \cdot \overset{..}{\underset{..}{Cl}} : \ = \ Na^+ \ \ : \overset{..}{\underset{..}{Cl}} : ^-$$

In a *covalent linkage* two atoms X and Y *share a pair of electrons*. Usually one electron of the shared pair is provided by each atom, thus :

$$: \overset{..}{X} \cdot + \cdot \overset{..}{Y} : \ = \ : \overset{..}{X} : \overset{..}{Y} :$$

$$\underset{\text{shared electrons}}{\uparrow}$$

For example, $: \overset{..}{\underset{..}{Cl}} \cdot + \cdot \overset{..}{\underset{..}{Cl}} : \ = \ : \overset{..}{\underset{..}{Cl}} : \overset{..}{\underset{..}{Cl}} :$

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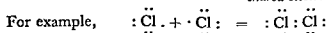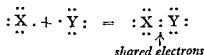
[1] In this book this policy has been followed only in the chapters dealing with organic chemistry, where it is particularly important to distinguish between electrovalent and covalent links.

The Periodic Classification of the Elements

Group	I	II	III	IV	V	VI	VII	VIII			I	II	III	IV	V	VI	VII	O
Subgroup	A	A	A	A	A	A	A	A	B	C	B	B	B	B	B	B	B	
	H 1																	He 2
First short period	Li 3	Be 4											B 5	C 6	N 7	O 8	F 9	Ne 10
Second short period	Na 11	Mg 12											Al 13	Si 14	P 15	S 16	Cl 17	A 18
First long period	K 19	Ca 20	Sc 21	Ti 22	V 23	Cr 24	Mn 25	Fe 26	Co 27	Ni 28	Cu 29	Zn 30	Ga 31	Ge 32	As 33	Se 34	Br 35	Kr 36
Second long period	Rb 37	Sr 38	Y 39	Zr 40	Nb 41	Mo 42	Ma 43	Ru 44	Rh 45	Pd 46	Ag 47	Cd 48	In 49	Sn 50	Sb 51	Te 52	I 53	Xe 54
Rare Earth period	Cs 55	Ba 56	RE* 57–71	Hf 72	Ta 73	W 74	Re 75	Os 76	Ir 77	Pt 78	Au 79	Hg 80	Tl 81	Pb 82	Bi 83	Po 84	— 85	Rn 86
Last period	— 87	Ra 88	Ac 89	Th 90	Pa 91	U 92												

The number under the symbol of each element is its Atomic Number. Elements discussed in this book are indicated in black type thus **H**.

* Rare Earth metals.

frequently of 8 electrons) in its outermost shell (see below). If two elements have the same numbers of electrons in their outermost shells, they show, in general, similar chemical properties. Modern physical evidence regarding electronic structures supports thoroughly the Periodic Classification, originally put forward on chemical evidence long before anything was known about the structure of the atom.

CHEMICAL BONDS

Purely chemical studies in the nineteenth century gave some evidence regarding the ways in which atoms are bound together in molecules by valency bonds. The valency of an element was one of the chief criteria for determining its place in the Periodic Table. So far as elementary organic chemistry is concerned, the valency ideas of the nineteenth century are largely adequate to-day. In inorganic chemistry, however, the picture has changed greatly.

There are two chief types of chemical linkage, viz., the *electrovalent*

ion A^-. The process may be represented as follows, the electrons in the outermost shell (valency electrons) being shown by dots :

$$B \cdot + \cdot \ddot{A} : \rightleftharpoons B^+ \quad : \ddot{A} : ^-$$

An electrovalent linkage is *always ionic* in solution, in the liquid, and

reactive metals have one, two or three electrons only in their outermost shells and tend to lose these. The atoms of the more reactive non-metals have one, two or : in their outermost shell a group of eight. Thus follows :

$$Na \cdot + \cdot \ddot{C}l : \rightleftharpoons Na^+ \quad : \ddot{C}l : ^-$$

In a *covalent linkage* two atoms X and Y *share a pair of electrons.* Usually one electron of the shared pair is provided by each atom, thus :

$$: \ddot{X} \cdot + \cdot \ddot{Y} : \rightleftharpoons : \ddot{X} \overset{\uparrow}{\underset{shared\ electrons}{:}} \ddot{Y} :$$

For example, $: \ddot{C}l \cdot + \cdot \ddot{C}l : \rightleftharpoons : \ddot{C}l : \ddot{C}l :$

[1] In this book this policy has been followed only in the chapters dealing with organic chemistry, where it is particularly important to distinguish between electrovalent and covalent links.

of analytical value because of their colour, *e.g.*, the cuprammonium ion $[Cu.4NH_3]^{++}$, or because of their solubility (see pp. 87-88).

VALENCY

The valency of an element (or number of valency bonds formed by it) and the relation of this to the Periodic Table may now be considered. In the simplest cases the valency is *either* the same as the Periodic Group number, *or* 8 minus the Periodic Group number. The reactive metals of Subgroups I A and II A at the extreme left of the Periodic Table can attain a stable electronic arrangement by *losing* their one or two outer electrons and forming univalent or divalent positive ions. They therefore show valencies of 1 and 2 respectively, and nearly always form electrovalent links. The non-metals of Subgroups VII B, VI B and V B at the right-hand side of the Periodic Table conversely can attain a stable electronic arrangement by *gaining* one, two or three electrons. This they do *either* by forming 1, 2 or 3 electrovalent links and becoming anions (as in sodium chloride Na^+Cl^- or calcium sulphide $Ca^{++}S^{--}$) *or* by sharing electrons and forming 1, 2 or 3 covalent links (as in their hydrides HCl, H_2S, H_3N, in many organic compounds $CH_3.Cl$, $CH_3.O.CH_3$, $CH_3.NH_2$, and in other compounds, *e.g.*, PCl_3). In either case the valency of the element is 8 *minus* the Periodic Group number. Many of these elements also show a valency equal to the Group Number in their highest oxides and related compounds, thus:
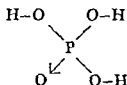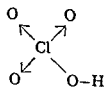
In these formulae the chlorine, sulphur and phosphorus atoms provide 7, 6, and 5 valency electrons respectively.

Many non-metals also show valencies intermediate between the two Group Valencies; usually successive valencies differ by two units from each other. ⁔ʰⁱ ‧ ‧ ‧ ‧ ‧ ‧ ‧
of 2 and 6, shows . ‧ ‧ ‧ ‧ ‧ ‧
electrons (called a

The lone pair of electrons is represented by two dots.

F

Covalent linkages are *non-ionic*. Linkages of this kind are formed most often between two non-metallic atoms. The C—C, C—H, C—O, C—N, C—Halogen links, which are the most important links in organic compounds, are all of this type ; most organic compounds therefore do not ionise.

Although covalent linkages are not ionic some of them may be turned into electrovalent linkages in certain conditions. For example, hydrogen and chlorine in hydrogen chloride gas are covalently-linked H : C̈l : If hydrogen chloride is dissolved in water, giving hydrochloric acid, the covalent linkage between hydrogen and chlorine is turned into an *electrovalent* linkage and the molecule ionises thus :

$$\text{H} : \overset{..}{\underset{..}{\text{Cl}}} : \quad \rightleftharpoons \quad \text{H}^+ + : \overset{..}{\underset{..}{\text{Cl}}} : ^-$$
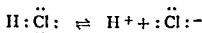
Links of this kind, which may be either electrovalent or covalent, are usually links between hydrogen and another non-metal.

In some covalent linkages the two electrons joining a pair of atoms are both provided by one atom. These are called *dative covalent linkages* or *co-ordinate links*. Dative linkages are *not* ionic.

When hydrogen chloride dissolves in water and ionises as shown above, the hydrogen ion is immediately linked by a *dative covalent linkage* to a water molecule giving the ion $[\text{H}_3\text{O}]^+$, thus :

$$\text{H} : \overset{..}{\underset{..}{\text{O}}} : \text{H} \; + \; \text{H}^+ \; = \; \left[\text{H} : \overset{..}{\underset{\text{H}}{\text{O}}} : \text{H} \right]^+ , \text{ also written } \left[\begin{matrix} \text{H—O—H} \\ \downarrow \\ \text{H} \end{matrix} \right]^+$$
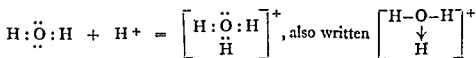
The two electrons which link the hydrogen ion with the water molecule are both provided by the oxygen of the latter. The dative covalent linkage is represented in formulae by an arrow, with its head pointing towards the atom which receives electrons.

In salt hydrates (*e.g.,* copper nitrate $\text{Cu(NO}_3)_2, 4\text{H}_2\text{O}$) the water molecules may be joined to the ions, usually the cation, by dative linkages both in the solid state and in solution :

$$\left[\begin{matrix} \text{H}_2\text{O} & & \text{OH}_2 \\ & \searrow \quad \swarrow & \\ & \text{Cu} & \\ & \nearrow \quad \nwarrow & \\ \text{H}_2\text{O} & & \text{OH}_2 \end{matrix} \right]^{++} \quad 2 \, \text{NO}_3^-$$
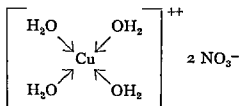
Numerous complex compounds of metals with ammonia and with various organic substances contain these linkages. Many of them are
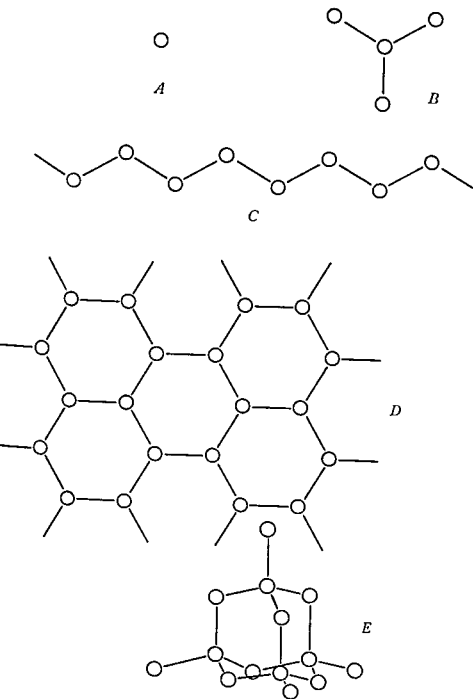
FIG. 6, 1
Types of Molecules and Ions

Carbon is almost invariably quadrivalent, and in practically every case all its four linkages are covalent. The peculiar nature of organic chemistry is largely due to the fact that carbon atoms alone are able to link themselves by stable covalent linkages in chains of any length.

The B Subgroup Metals (Subgroups I B to IV B) usually show their group valencies, forming cations (Ag^+, Zn^{++}, Sn^{++++}), although they also form many covalent compounds. Tin, lead and copper commonly show abnormal valencies of 2. (For explanations see other books.)

The elements in the middle of the Periodic Table, the Transition Elements in the wider sense (Subgroups III A to VII A and VIII), show very variable valencies. In nearly every case the highest valency, often shown in an oxygen compound, is the same as the Group Number, but in most cases the commonest compounds are those in which the elements show valencies of 2 or 3, irrespective of their Group Number. For details see other books (*e.g.*, Sidgwick, *The Electronic Theory of Valency*, Oxford); for simple examples see the sections in this book on chromium and manganese (pp. 254-256 and 267-269).

TYPES OF MOLECULES AND IONS

The following table summarises the different types of molecules and ions, *i.e.*, the smallest units of substances which can have an independent existence, and gives examples of each.

Molecules	Ions
Monatomic molecules Argon, A	*Monatomic ions* Sodium, Na^+ Chloride, Cl^-
Small polyatomic molecules Hydrogen, H_2 Ammonia, NH_3 Methane, CH_4 Pentane, $CH_3(CH_2)_3.CH_3$ and most organic compounds	*Small polyatomic ions* Sulphate, SO_4^{--} Cuprammonium $[Cu.4NH_3]^{++}$ Acetate, $CH_3.COO^-$
Large polyatomic molecules One-dimensional (chain) Cellulose Two-dimensional (sheet) Graphite Three-dimensional (network) Diamond	*Large polyatomic ions* One-dimensional (chain) Asbestos Two-dimensional (sheet) Mica Three-dimensional (network) Felspar

GENERAL APPLICATION TO ELECTROLYTES

6, 7   APPLICATION OF THE LAW OF MASS
ACTION TO ELECTROLYTES

Since *strong* electrolytes are 100% dissociated in aqueous solution, there is no equilibrium between their ions and undissociated molecules to consider.

The Law of Mass Action may be applied to the dissociation of a *weak* electrolyte BA in solution.

$$BA \rightleftharpoons B^+ + A^-.$$

The concentrations of ions and undissociated molecules are always related by the expression

$$\frac{[B^+][A^-]}{[BA]} = K \qquad . \qquad . \qquad . \qquad (4)$$

where K is the *dissociation constant* of the electrolyte (see also pp. 93–95).

6, 8   THE SOLUBILITY OF SOLID ELECTROLYTES
IN WATER

STRONG ELECTROLYTES

$$B^+A^-B^+A^-B^+A^-B^+$$
$$A^-B^+A^-B^+A^-B^+A^-$$
$$B^+A^-B^+A^-B^+A^-B^+$$

FIG. 6, 2

Surface of a Solid Strong Electrolyte

Fig. 6, 2 represents the surface of a solid strong electrolyte in contact with its saturated aqueous solution.[1] Suppose the surface contains x A⁻ ions and y B⁺ ions. The following four processes are going on at the rates (r_1, etc.) indicated by the equations (k_1, etc. are constants).

Process	Rate
A⁻ ions dissolve from the surface of the solid.	$r_1 = k_1 x$
A⁻ ions ... to the	$r_2 = k_2 . y . [A^-]$
B⁺	$r_3 = k_3 . y$
B⁺	$r_4 = k_4 . x . [B^+]$
points where A⁻ ions are exposed.	

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[1] This section is based on the treatment used by Smith, *Analytical Processes —A Physico-Chemical Interpretation*, Arnold, 1940

Monatomic molecules (Fig. 6, 1, A) are rare. Each atom has an independent existence in gas, liquid or solid. Small polyatomic molecules (Fig. 6, 1, B) include the non-ionised inorganic compounds and the great majority of organic compounds. In these the atoms of each molecule are bound together by covalent linkages, and the molecule as a whole is independent in gas, liquid or solid. The molecular weights of substances of these types can be determined by the "classical" methods, viz.: osmotic pressure, depression of the freezing-point, vapour density (if volatile).

Monatomic ions and small polyatomic ions, which correspond in structure to the above, are charged and can exist only along with ions carrying an equal total number of charges of opposite sign. The individual atoms of polyatomic ions are joined to one another by covalent links. In the solid state positive and negative ions are disposed alternately in regular patterns. Substances consisting of these ions are usually met as solids or in aqueous solution. Much of elementary inorganic chemistry is concerned with the reactions of these ions in solution.

The large molecules and ions have not in the past been given due attention in elementary books, since it is only within recent years that investigation of their structures (by X-ray and other methods) has been possible. Many of these large molecules and ions can exist only in the solid state. Others can exist in colloidal solution, e.g., some polysaccharides, most proteins. They consist of series of units covalently-linked in a regular pattern in one, two or three dimensions (Fig. 6, 1, C, D and E).

The physical characteristics of these substances depend closely on the molecular pattern. Substances containing one-dimensional polymers are fibrous, e.g., asbestos (a silicate), cellulose, keratin (a protein). Two-dimensional polymers tend to cleave easily, e.g., mica, talc (silicates), graphite. Three-dimensional polymers are often hard, e.g., diamond, silica, felspars (silicates) and some synthetic plastics. In most ionised compounds of this type only one kind of ion (either positive or negative) is large, and the ions of opposite charge are small.

These large molecules and ions can usually be broken down to single units which have quite different properties, e.g., cellulose may be hydrolysed to glucose (soluble in water), and insoluble silicates may be transformed by fusion with sodium carbonate into sodium silicate (soluble in water) and various metallic carbonates ("soluble" in dilute acid). Some large molecules may be made by polymerising the small units; most synthetic plastics are made in this way.

One type of material not included in the above classification is the metal. Metals (solid or liquid) and alloys may be looked on as collections of positive ions surrounded by a "cloud" of free electrons sufficient to neutralise the positive ions; for example, sodium metal might be represented as $Na^+ + e$.

GENERAL APPLICATION TO ELECTROLYTES

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$$BA \rightleftharpoons B^+ + A^-.$$

The concentrations of ions and undissociated molecules are always related by the expression

$$\frac{[B^+][A^-]}{[BA]} = K \qquad . \qquad . \qquad . \qquad (4)$$

where K is the *dissociation constant* of the electrolyte (see also pp. 93-95).

6, 8 THE SOLUBILITY OF SOLID ELECTROLYTES IN WATER

STRONG ELECTROLYTES
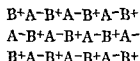
B⁺A⁻B⁺A⁻B⁺A⁻B⁺
A⁻B⁺A⁻B⁺A⁻B⁺A⁻
B⁺A⁻B⁺A⁻B⁺A⁻B⁺

FIG. 6, 2

Surface of a Solid Strong Electrolyte

Fig. 6, 2 represents the surface of a solid strong electrolyte in contact with its saturated aqueous solution.[1] Suppose the surface contains x A⁻ ions and y B⁺ ions. The following four processes are going on at the rates (r_1, etc.) indicated by the equations (k_1, etc. are constants).

Process	Rate	
A⁻ ions dissolve from the surface of the solid	r_1	$= k_1.x$
A⁻ ions adhere to the surface of the solid, at the points where B⁺ ions are exposed.	r_2	$= k_2.y.[A^-]$
B⁺ ions dissolve from the surface of the solid	r_3	$= k_3.y$
B⁺ ions adhere to the surface of the solid, at the points where A⁻ ions are exposed.	r_4	$= k_4.x.[B^+]$

[1] This section is based on the treatment used by Smith, *Analytical Processes —A Physico-Chemical Interpretation*, Arnold, 1940.

Since the solid and the saturated solution are in equilibrium $r_2 = r_2$ and $r_3 = r_4$,

therefore

$$h_1 x = k_2 \cdot y \cdot [A^-]$$

and

$$h_3 \cdot y = k_4 \cdot x \cdot [B^+].$$

Hence

$$\frac{x}{y} = \frac{k_2 \cdot [A^-]}{k_1} = \frac{k_3}{k_4 \cdot [B^+]};$$

eliminating x and y which are unknown,

$$[B^+] \cdot [A^-] = \frac{h_1 k_3}{k_2 k_4} = K_s \quad . \quad . \quad (5)$$

K_s is a constant and is called the *solubility product* of BA. A solution in which the product of $[B^+]$ and $[A^-]$ momentarily exceeds K_s is unstable, and will deposit solid BA until the product $[B^+] \cdot [A^-]$ is reduced to K_s. Such a solution may be produced by mixing two substances, each of which contains one of the two ions in sufficient concentration.

WEAK ELECTROLYTES

By reasoning similar to that used in considering the solubility of a non-ionising substance (p. 74) and in considering the equilibrium between non-ionised molecules and ions of an electrolyte (p. 85), it may be shown that for a weak electrolyte CD in solution

$$[C^+] \cdot [D^-] = \text{constant.}$$

INSOLUBLE SUBSTANCES

The term " insoluble " demands a word of explanation. Strictly speaking, no substance is *completely insoluble* in any solvent. In many cases, however, the solubility is almost negligible, *e.g.*, many salts (*e.g.*, barium sulphate, silver chloride, copper sulphide) have solubilities ranging from 10^{-4} to 10^{-20} gram-molecules per litre. These salts should be described as " very sparingly soluble," but the habit of calling them " insoluble " is of too long standing to be broken now.

6, 9   THE COMMON ION EFFECT

The common ion effect is an important example of interference with a dynamic equilibrium.

Precipitation of a Strong Electrolyte by a Common Ion.

Consider a saturated solution of sodium chloride. The equilibrium between the solid and the dissolved ions has been discussed above. The concentrations of the ions are given by the equation $[Na^+] \cdot [Cl^-] = K_s$. Suppose that to this solution is added a concentrated solution of a very soluble compound giving rise to sodium or

chloride ions. The product $[Na^+].[Cl^-]$ momentarily exceeds K_s, and sodium and chloride ions come out of solution at an increased rate until the product is reduced to K_s once more, *i.e.*, more solid sodium chloride is formed. An experiment illustrating this effect is described on p. 161.

Repression of the Ionisation of a Weak Electrolyte by a Common Ion.

If to a solution of a weak electrolyte XA is added a strong electrolyte containing a common ion (B^+A^-) the dissociation of the weak electrolyte is decreased. For the solution of

$$XA \rightleftharpoons X^+ + A^-$$

$$\frac{[X^+].[A^-]}{[XA]} = K_{XA}.$$

If $[A^-]$ is increased by the addition of B^+ and A^-, $[X^+]$ will be decreased and $[XA]$ increased to produce a new state of equilibrium in which the *percentage* of XA *ionised* will be *less* than before.

Two instances of this effect are provided in the Group Separation in qualitative analysis; first, the addition of hydrochloric acid to decrease the ionisation of hydrogen sulphide for the precipitation of Group 2; secondly, the addition of ammonium chloride to decrease the ionisation of ammonium hydroxide in the precipitation of Group 3. For experiment see pp. 161-162.

6, 10   COMPLEX IONS

Complex ions containing water molecules or ammonia molecules attached to a metallic atom by dative covalent links have been mentioned in the section on valency (pp. 80-81). The formation of complex ions [1] provides further examples of the disturbance of ionic equilibria. In many cases the solubilities of ammonia complex salts differ from those of the corresponding water complex salts or the simple salts. Silver chloride, Ag^+Cl^-, is virtually insoluble; the chloride of the silver ammonia complex ion, $[Ag.2NH_3]^+Cl^-$, is soluble. Cupric hydroxide, $Cu^{++}[OH]^-_2$, or $[Cu.4H_2O]^{++}[OH]^-_2$, is insoluble; the hydroxide of the cuprammonium complex, $[Cu.4NH_3]^{++}[OH]^-_2$, is soluble. Thus many compounds (*e.g.*, silver chloride, cupric hydroxide) which are virtually insoluble in water are "soluble" in dilute ammonium hydroxide due to the formation of ammonia-complex ions.

Another type of complex ion is that in which a metal forms part

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[1] "Square brackets" are used in chemical literature both to indicate concentrations in gram-molecular constituents of a complex ion: *thick* square brackets thus $[\ \ ]$ (or gram-ions) per litre; thin constituents of a complex ion.

Since the solid and the saturated solution are in equilibrium $r_1=r_2$ and $r_2=r_4$,

therefore $$h_1.x = k_2.y.[A^-]$$

and $$k_3.y = k_4.x.[B^+].$$

Hence $$\frac{x}{y} = \frac{k_2.[A^-]}{k_1} = \frac{k_3}{k_4.[B^+]};$$

eliminating x and y which are unknown,

$$[B^+].[A^-] = \frac{k_1 k_3}{k_2 k_4} = K_s \quad . \quad . \quad . \quad (5)$$

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6, 9   THE COMMON ION EFFECT

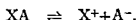The common ion effect is an important example of interference with a dynamic equilibrium.

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$$XA \rightleftharpoons X^+ + A^-.$$

$$\frac{[X^+].[A^-]}{[XA]} = K_{XA}.$$

If $[A^-]$ is increased by the addition of B^+ and A^-, $[X^+]$ will be decreased and $[XA]$ increased to produce a new state of equilibrium in which the *percentage* of XA *ionised* will be *less* than before.

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[1] " Square brackets " a⁻ ⸱ ⸱ ⸱ ⸱ ⸱ ⸱
centrations in gram-mole⸱ ⸱ ⸱ ⸱
constituents of a complex i ⸱ ⸱ ⸱ ⸱
thick square brackets thus ⸱ ⸱ ⸱
(or gram-ions) per litre ; ⸱ ⸱ ⸱
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Since the solid and the saturated solution are in equilibrium $r_1 = r_2$ and $r_3 = r_4$.

therefore

$$k_1 x = k_2 y \cdot [A^-]$$

and

$$k_3 y = k_4 x \cdot [B^+].$$

Hence

$$\frac{x}{y} = \frac{k_2 \cdot [A^-]}{k_1} = \frac{k_3}{k_4 \cdot [B^+]};$$

eliminating x and y which are unknown,

$$[B^+] \cdot [A^-] = \frac{k_1 k_3}{k_2 k_4} = K_s \quad . \quad . \quad . \quad (5)$$

K_s is a constant and is called the *solubility product* of BA. A solution in which the product of $[B^+]$ and $[A^-]$ momentarily exceeds K_s is unstable, and will deposit solid BA until the product $[B^+].[A^-]$ is reduced to K_s. Such a solution may be produced by mixing two substances, each of which contains one of the two ions in sufficient concentration.

WEAK ELECTROLYTES

By reasoning similar to that used in considering the solubility of a non-ionising substance (p. 74) and in considering the equilibrium between non-ionised molecules and ions of an electrolyte (p. 85), it may be shown that for a weak electrolyte CD in solution

$$[C^+] \cdot [D^-] = \text{constant}.$$

INSOLUBLE SUBSTANCES

The term " insoluble " demands a word of explanation. Strictly speaking, no substance is *completely insoluble* in any solvent. In many cases, however, the solubility is almost negligible, *e.g.*, many salts (*e.g.*, barium sulphate, silver chloride, copper sulphide) have solubilities ranging from 10^{-4} to 10^{-20} gram-molecules per litre. These salts should be described as " very sparingly soluble," but the habit of calling them " insoluble " is of too long standing to be broken now.

6, 9   THE COMMON ION EFFECT

The common ion effect is an important example of interference with a dynamic equilibrium.
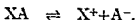
Precipitation of a Strong Electrolyte by a Common Ion.

Consider a saturated solution of sodium chloride. The equilibrium between the solid and the dissolved ions has been discussed above. The concentrations of the ions are given by the equation $[Na^+].[Cl^-] = K_s$. Suppose that to this solution is added a concentrated solution of a very soluble compound giving rise to sodium or

chloride ions. The product $[Na^+].[Cl^-]$ momentarily exceeds K_s, and sodium and chloride ions come out of solution at an increased rate until the product is reduced to K_s once more, *i.e.*, more solid sodium chloride is formed. An experiment illustrating this effect is described on p. 161.

Repression of the Ionisation of a Weak Electrolyte by a Common Ion.

If to a solution of a weak electrolyte XA is added a strong electrolyte containing a common ion (B^+A^-) the dissociation of the weak electrolyte is decreased. For the solution of XA

$$XA \rightleftharpoons X^+ + A^-.$$

$$\frac{[X^+].[A^-]}{[XA]} = K_{XA}.$$

If $[A^-]$ is increased by the addition of B^+ and A^-, $[X^+]$ will be decreased and $[XA]$ increased to produce a new state of equilibrium in which the *percentage* of XA ionised will be *less* than before.

Two instances of this effect are provided in the Group Separation in qualitative analysis; first, the addition of hydrochloric acid to decrease the ionisation of hydrogen sulphide for the precipitation of Group 2; secondly, the addition of ammonium chloride to decrease the ionisation of ammonium hydroxide in the precipitation of Group 3. For experiment see pp. 161-162.

6, 10   COMPLEX IONS

Complex ions containing water molecules or ammonia molecules attached to a metallic atom by dative covalent links have been mentioned in the section on valency (pp. 80-81). The formation of complex ions [1] provides further examples of the disturbance of ionic equilibria. In many cases the solubilities of ammonia complex salts differ from those of the corresponding water complex salts or the simple salts. Silver chloride, Ag^+Cl^-, is virtually insoluble; the chloride of the silver ammonia complex ion, $[Ag.2NH_3]^+Cl^-$, is soluble. Cupric hydroxide, $Cu^{++}[OH]^-_2$, or $[Cu.4H_2O]^{++}[OH]^-_2$, is insoluble; the hydroxide of the cuprammonium complex, $[Cu.4NH_3]^{++}[OH]^-_2$, is soluble. Thus many compounds (*e.g.*, silver chloride, cupric hydroxide) which are virtually insoluble in water are " soluble " in dilute ammonium hydroxide due to the formation of ammonia-complex ions.

Another type of complex ion is that in which a metal forms part

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[1] " Square brackets " are ~~~ ~~ ~~ ~~~~ ~~ ~~~~~~~ ~ ~~ ~~~~~~ centrations in gram-molec~~~
constituents of a complex io~ .   .
thick square brackets thus [H₂S] indicate a concentration in gram-molecules (or gram-ions) per litre; *thin* square brackets thus $[Cu.4NH_3]^{++}$ enclose the constituents of a complex ion.

Since the solid and the saturated solution are in equilibrium $r_1 = r_2$ and $r_3 = r_4$,

therefore

$$k_1 x = k_2 y . [A^-]$$

and

$$k_3 y = k_4 x . [B^+].$$

Hence

$$\frac{x}{y} = \frac{k_2 . [A^-]}{k_1} = \frac{k_3}{k_4 . [B^+]};$$

eliminating x and y which are unknown,

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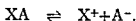
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Another type of complex ion is that in which a metal forms part

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[1] " Square brackets " are used in chemical literature both to indicate concentrations in gram-molecules or gram-ions per litre and to enclose the constituents of a complex ion In this book the following distinction is made : *thick* square brackets thus [H₂S] indicate a concentration in gram-molecules (or gram-ions) per litre ; *thin* square brackets thus [Cu.4NH₃]⁺⁺ enclose the constituents of a complex ion.

of an anion. If an iodide solution is added to a mercuric salt solution, a red precipitate of mercuric iodide is formed,

$$Hg^{++} + 2I^- \rightleftharpoons HgI_2 \downarrow.$$
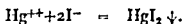
If more iodide is then added, the red precipitate disappears, giving a colourless solution; mercuric iodide reacts with excess iodide ions, forming the complex mercuri-iodide ion $[HgI_4]^{--}$, the potassium salt of which is soluble.

$$HgI_2 + 2I^- \rightleftharpoons [HgI_4]^{--}.$$
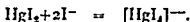
Important examples of this type of complex ion are the ferrocyanides and ferricyanides.

Anions containing a metallic atom are also formed by certain metallic hydroxides which are *amphoteric*, *i.e.*, which may act either as acids or bases. For example, aluminium hydroxide is virtually insoluble in water. If treated with a strong acid, *e.g.*, hydrochloric acid, it dissolves, forming aluminium chloride.

$$\begin{matrix} HO \quad\quad OH^* \\ \diagdown \quad \diagup \\ Al \\ | \\ OH \end{matrix} \quad + 3H^+ + 3Cl^- = Al^{+++} + 3Cl^- + 3HOH.$$
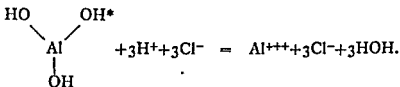
If, on the other hand, aluminium hydroxide is treated with a caustic alkali, it dissolves, forming an aluminate, in which aluminium forms part of a complex anion.

$$\begin{matrix} HO \quad\quad OH^* \\ \diagdown \quad \diagup \\ Al \\ | \\ OH \end{matrix} \quad + 3Na^+ + 3OH^- \rightleftharpoons [AlO_3]^{---} + 3Na^+ + 3HOH.$$
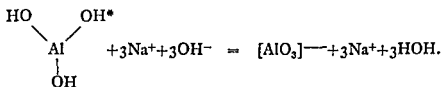
* These formulae might be written $Al(OH)_3$ and H_3AlO_3 respectively, to show that in the first case the compound is acting as a base, and in the second case as an acid.

6, 11   SOLUBILITY PRODUCTS IN ANALYSIS

The precipitation of any insoluble or sparingly soluble electrolyte as a result of the mixing of two solutions, each of which contains one of its ions, provides a qualitative test for each of the two ions concerned.[1]

The great majority of the tests used in simple inorganic analysis are precipitations of this type, *e.g.*,

$$Ag^+ + Cl^- = AgCl \downarrow.$$
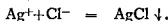
In this example a solution of any soluble silver salt may be used as a testing reagent for chlorides, while a solution of any soluble chloride

[1] In many cases it also provides a method for the quantitative determination of the ions ; see precipitation titrations, pp. 149-152.

may be used as a testing reagent for silver salts. Furthermore, the precipitation of silver chloride may be used to determine each of the two ions, either gravimetrically or volumetrically. The majority of the tests used in inorganic qualitative analysis are of this type. In fact it may almost be said that the basis of inorganic qualitative analysis is a knowledge of the solubilities of salts.

If a salt has a very *low solubility product*, this is exceeded when very dilute solutions of the appropriate reagents are mixed; the precipitation of the salt therefore provides a *very sensitive test* for its ions. If a salt has a relatively *high solubility product*, this is exceeded only when more concentrated solutions of the reagents are mixed; in this case the *test* is relatively *insensitive*.

The following are representative solubility products at room temperature:

Salt	Solubility Product		Precipitation Test for Ions
$AgCl$	$[Ag^+].[Cl^-]$	$= 1 \cdot 2 \times 10^{-10}$	
Ag_2CrO_4	$[Ag^+]^2.[CrO_4^{--}]$	$= 1 \cdot 7 \times 10^{-12}$	
AgI	$[Ag^+].[I^-]$	$= 1 \cdot 7 \times 10^{-16}$	Sensitive.
$BaSO_4$	$[Ba^{++}].[SO_4^{--}]$	$= 1 \cdot 2 \times 10^{-10}$	
CuS	$[Cu^{++}].[S^{--}]$	$= 8 \cdot 5 \times 10^{-45}$	
$CaSO_4$	$[Ca^{++}].[SO_4^{--}]$	$= 2 \cdot 3 \times 10^{-4}$	Not
$PbCl_2$	$[Pb^{++}].[Cl^-]^2$	$= 2 \cdot 4 \times 10^{-4}$	sensitive.

INDICATORS IN PRECIPITATION TITRATIONS

The use of indicators in certain precipitation titrations depends upon the relative solubilities of the salts concerned. The use of chromate as indicator in the titration of chlorides with silver nitrate will be taken as an example. Silver chloride ($AgCl$) is white, silver chromate (Ag_2CrO_4) is red; both are sparingly soluble in water—silver chloride more sparingly than silver chromate. If silver nitrate solution is added gradually to a chloride solution containing a little chromate as indicator, nearly *all* the chloride is precipitated as white silver chloride before any *permanent* formation of red silver chromate occurs. When the precipitation of chloride as silver chloride is almost complete, the next drop of silver nitrate solution will produce a red precipitate of silver chromate. The *first formation of a permanent* pink or red colour in the mixture therefore means that practically all the chloride has been precipitated, and marks the end-point when the reaction is used in a titration.

For a mathematical treatment of this problem using the solubility products of the salts, see larger books (*e.g.*, Vogel, *Quantitative Inorganic Analysis*, 1944, pp. 90–91).

The use of a ferric salt as indicator in silver thiocyanate titrations depends on similar principles. Ferric ions and thiocyanate ions combine on mixing to give blood-red complex ferri-thiocyanate ions.[1]

$$Fe^{+++} + 6SCN^- \rightleftharpoons [Fe(SCN)_6]^{---}.$$

In the titrations a small quantity of a ferric salt solution is added to the solution containing silver ions. The thiocyanate solution is then added gradually to this. So long as an appreciable quantity of silver ions is present in the mixture, white silver thiocyanate is precipitated; when nearly all the silver has been precipitated, the next drop of thiocyanate solution reacts with the ferric salt to form red ferri-thiocyanate ions. In the Volhard chloride determination silver chloride must be removed by filtration, because, if present, it would react slowly with ferri-thiocyanate ions thus:

$$6AgCl + [Fe(SCN)_6]^{---} = 6AgSCN + Fe^{+++} + 6Cl^-$$

and the red colour of the ferri-thiocyanate would fade slowly. In the corresponding determinations of bromide and iodide the halides need not be filtered off, since they do not react with ferri-thiocyanate ions.

THE GROUP SEPARATION OF THE CATIONS

The separation of the cations into groups in the usual method of analysis depends upon the fractional precipitation of the sulphides.[2] The cations are divided into three main classes according to the solubilities of their sulphides, viz.:

Class A.   Groups 1 and 2.   Sulphides very sparingly soluble; precipitated by H_2S even in acid solution.

Class B.   Groups 3 and 4.   Sulphides less sparingly soluble; precipitated by H_2S in alkaline but *not* in acid solution.

Class C.   Groups 5 and 6.   Sulphides soluble in water (or hydrolysed); *never* precipitated by H_2S.

The precipitation of a few chlorides by hydrochloric acid in Group 1, and the precipitation of a few hydroxides by ammonium hydroxide in Group 3 should be looked upon as incidental to the main precipitations with hydrogen sulphide in acid and in alkaline solution respectively.

The following discussion[3] shows how sulphides whose solubility product is very small (*e.g.*, CuS, 8.5×10^{-45}) fall into Class A, while

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[1] The colour was formerly thought to be due to non-ionised ferric thiocyanate.

[2] The remainder of this section is largely based on the treatment used by Brewer, *Elementary Quantitative Analysis*, Oxford, 1933.

[3] The treatment is much simplified since it does not take account of the fact that hydrogen sulphide, being a dibasic acid, ionises in two stages.

those whose solubility product is somewhat greater (*e.g.*, ZnS, 1.0×10^{-20}) fall into Class B. Suppose that to a solution containing $0.1M$ copper sulphate and $0.1M$ zinc sulphate, sufficient hydrochloric acid is added to make $[H^+]=0.25$ (the usual figure in qualitative analysis), and the solution is then saturated with hydrogen sulphide; calculation shows that the sulphide ion concentration $[S^{--}]$ is 1.7×10^{-22}. The product $[Cu^{++}][S^{--}]$ is then $0.1 \times 1.7 \times 10^{-22} = 1.7 \times 10^{-23}$; this is vastly greater than the solubility product of copper sulphide, and the latter is therefore precipitated. The product $[Zn^{++}][S^{--}]$ is also 1.7×10^{-23}; this, however, is less than the solubility product of zinc sulphide, and the latter is *not* precipitated. If the copper sulphide is filtered off, ammonium chloride and ammonium hydroxide added as for Group 4, all the hydrogen sulphide in solution is transformed into ionised ammonium sulphide, and $[S^{--}]$ is of the order of 10^{-2}. The product $[Zn^{++}][S^{--}]=0.1 \times 10^{-2}=10^{-3}$, which greatly exceeds the solubility product of zinc sulphide. The latter is therefore precipitated.

The Cation Separation and the Periodic Table.

If the Cation Separation is considered in this light it may be seen that, contrary to common belief, there is a connection between it and the Periodic Table.

Class A consists of metals in Periodic Subgroups I B to V B (*i.e.*, the " right centre " of the Periodic Table.

Class B consists of metals in Periodic Subgroups III A to VII A and VIII (*i.e.*, the " left centre " of the Periodic Table).[1]

Class C consists of metals in Periodic Subgroups I A and II A (*i.e.*, the " extreme left " of the Periodic Table).

Analytical Precipitates and Natural Occurrence of Metals.

It is of interest that most metals occur in nature as minerals which, apart from silicates, are of the same character as the precipitates in which the metals are found in analysis (*e.g.*, lead, copper and zinc as sulphides, iron and aluminium as hydroxides, calcium and magnesium as carbonates). The obvious explanation is that only water-insoluble compounds can withstand the weathering actions to which minerals are submitted in nature.

HYDROGEN-ION AND HYDROXYL-ION CONCENTRATIONS

Sections 6, 12 to 6, 19 (pp. 92–112) deal with the concentrations in aqueous solutions of hydrogen and hydroxyl ions. These ions are present in all aqueous solutions, being produced in small quantities

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[1] Also zinc (Periodic Subgroup II B), which is an exception.

The use of a ferric salt as indicator in silver thiocyanate titrations depends on similar principles. Ferric ions and thiocyanate ions combine on mixing to give blood-red complex ferri-thiocyanate ions.[1]

$$Fe^{+++}+6SCN^- = [Fe(SCN)_6]^{---}.$$

In the titrations a small quantity of a ferric salt solution is added to the solution containing silver ions. The thiocyanate solution is then added gradually to this. So long as an appreciable quantity of silver ions is present in the mixture, silver thiocyanate is precipitated; when nearly all the silver has been precipitated, the next drop of thiocyanate solution reacts with the ferric salt to form red ferri-thiocyanate ions. In the Volhard chloride determination silver chloride must be removed by filtration, because, if present, it would react slowly with ferri-thiocyanate ions thus :

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---

[1] The colour was formerly thought to be due to non-ionised ferric thiocyanate.

concentrations are therefore usually described by means of the *negative logarithm of the concentration*.[1] This negative logarithm is called the *p*H; the relation between [H+] and *p*H is as follows :

$$pH = \log \frac{1}{[\text{H}^+]} = -\log [\text{H}^+] \quad . \quad (8)$$

or

$$[\text{H}^+] = 10^{-pH} \quad . \quad . \quad . \quad . \quad (9)$$

For example, if

$$[\text{H}^+] = 0.01 = 10^{-2}, \quad pH = -\log 10^{-2} = 2.$$

6, 13   STRENGTH OF ACIDS AND BASES

A *strong* acid or base is one which is 100% ionised in dilute aqueous solution, *e.g.*, the strong mineral acids (hydrochloric, nitric and sulphuric) and the caustic alkalis (sodium and potassium hydroxides).

A *weak* acid or base is one which in aqueous solution is ionised to a small extent. If HA represents a weak monobasic acid which ionises thus :

$$\text{HA} \rightleftharpoons \text{H}^+ + \text{A}^-,$$

the concentrations of HA molecules and of H+ and A− ions in any aqueous solution are related by the Mass Action expression

$$\frac{[\text{H}^+].[\text{A}^-]}{[\text{HA}]} = K_a \quad . \quad . \quad . \quad (10)$$

K_a is the *dissociation constant* of the acid HA. The dissociation constants of the important weak acids range from 10^{-2} to 10^{-10}. These figures themselves are inconvenient to use ; their negative logarithms (pK_a values) are therefore used instead.

$$pK_a = \log \frac{1}{K_a} = -\log K_a \quad . \quad (11)$$

$$K_a = 10^{-pK_a} \quad . \quad . \quad . \quad (12)$$

Each stage in the dissociation of a weak polybasic acid may be considered separately in the above way. See the discussion of a phosphoric acid titration on pp. 103-106 and 167.

Weak bases (*e.g.*, BOH) may be considered similarly.

$$\frac{[\text{B}^+].[\text{OH}^-]}{[\text{BOH}]} = K_b \quad . \quad . \quad . \quad (13)$$

$$pK_b = \log \frac{1}{K_b} = -\log K_b \quad . \quad . \quad (14)$$

pK values of weak acids and weak bases considered in the chapters on systematic inorganic chemistry and organic chemistry are given there.

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[1] All logarithms in this book are to base 10.

by the water itself and in larger quantities by other substances, viz., acids (producers of hydrogen ions) and bases (producers of hydroxyl ions) which may be present. These sections therefore deal with the general chemistry of acids and bases.

The behaviour of certain compounds which act both as acids and bases, *amphoteric electrolytes*, is considered elsewhere. Amphoteric metallic hydroxides have been discussed briefly on p. 88, while the amino acids and proteins, organic compounds containing both acidic and basic radicals, which are also amphoteric and are of very great physiological importance, are discussed on pp. 399-400.

6, 12   THE DISSOCIATION OF WATER. THE *p*H SCALE

Water dissociates to a very slight extent, forming hydrogen [1] and hydroxyl ions thus:
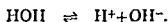
$$HOH \;\rightleftharpoons\; H^+ + OH^-.$$

The mass action expression for the equilibrium is

$$\frac{[H^+].[OH^-]}{[HOH]} \;=\; K \qquad . \qquad . \qquad . \qquad (6)$$

This may be written

$$[H^+].[OH^-] \;=\; K.[HOH].$$

Since water ionises to a very slight extent, [HOH] is virtually constant in dilute solutions; $K.[HOH]$ may therefore be replaced by another constant K_w. This constant, which is called the *ionic product of water*,[2] is approximately 10^{-14}.

$$[H^+].[OH^-] \;=\; K_w \;=\; 10^{-14} \qquad . \qquad . \qquad (7)$$

In pure water $[H^+] \;=\; [OH^-] \;=\; 10^{-7}.$

The equation $[H^+].[OH^-] = 10^{14}$ holds for all dilute solutions, even if acids or bases providing large concentrations of hydrogen or hydroxyl ions are present. An *acid* solution is one in which $[H^+] > 10^{-7}$; $[OH^-] < 10^{-7}$. An *alkaline* solution is one in which $[H^+] < 10^{-7}$; $[OH^-] > 10^{-7}$. A *neutral* solution is one in which $[H^+] = [OH^-] \approx 10^{-7}$. Since hydrogen- and hydroxyl-ion concentrations are related by equation (7), it is convenient to express degrees both of acidity and of alkalinity in terms of hydrogen-ion concentration.

Figures such as 10^{-7} or 0.0000001 are clumsy to use; hydrogen-ion

[1] The hydrogen ion is combined with a molecule of water, forming the hydroxonium ion H_3O^+. For the sake of simplicity, however, H^+ is used in equations instead of H_3O^+.
[2] This ionic product varies considerably with temperature. It is 0.3×10^{-14} at $10°$, 1.0×10^{-14} at $25°$, and 30×10^{-14} at $40°$. For all simple calculation the value 1.0×10^{-14} is used.

Dilute Solution of a Weak Base (e.g., *Ammonium Hydroxide*).

$$[OH^-] \approx \sqrt{K_b.[\text{base}]} \qquad . \qquad . \qquad . \qquad (21)$$

$$[H^+] = \frac{K_w}{\sqrt{K_b.[\text{base}]}} \; ; \; pH = 14 - \tfrac{1}{2}pK_b + \tfrac{1}{2}\log[\text{base}] \qquad (22)$$

For an experiment on the *p*H values of strong and weak acid solutions see pp. 164-165.

Attention must be drawn to the difference in meaning between the terms " strength," " strong " and " weak," which refer to the *degree of dissociation* of an electrolyte and the terms " concentration," " concentrated " and " dilute " which refer to the *amount* of a substance *per unit volume of solution.*

6, 14   SALT HYDROLYSIS

The student is familiar from elementary work with the fact that all salt solutions are not " neutral."

The *p*H value of any solution of a strong-acid strong-base salt (*e.g.*, sodium chloride) is equal to that of pure water, viz., 7·0. The *p*H values of solutions of a weak-acid strong-base salt (*e.g.*, sodium acetate) are above 7, while those of solutions of strong-acid weak-base salts (*e.g.*, ammonium chloride) are below 7. The *p*H values of solutions of weak-acid weak-base salts are in some cases above 7, in other cases below 7.

These facts may be explained as follows. When sodium acetate ($CH_3.COO-Na^+$) is dissolved in water, it dissociates completely, giving sodium cations and acetate anions. Since acetic acid is a weak acid, acetate and hydrogen ions cannot coexist in high concentrations; some acetate ions of the salt therefore combine with hydrogen ions of the water. Sodium hydroxide being a strong base, sodium ions of the salt do *not* combine with hydroxyl ions of the water. The process may be represented thus:

$$Na^+ + CH_3.COO- + H^+ + OH^- = CH_3.COOH + Na^+ + OH^-.$$

The hydroxyl-ion concentration of the solution is therefore greater than the hydrogen-ion concentration, and the *p*H of the solution is *greater than* 7. The extent to which combination between hydrogen ions and anions takes place depends on the strength of the weak acid.

The hydrogen-ion concentration and *p*H of solutions of salts such as sodium acetate can be calculated from the following equations, derived from equations (7) and (10), pp. 92-93 :

$$[H^+] = \sqrt{\frac{K_a.K_w}{[\text{salt}]}} \qquad . \qquad . \qquad . \qquad (23)$$

$$pH = 7 + \tfrac{1}{2}pK_a + \tfrac{1}{2}\log[\text{salt}] \qquad . \qquad . \qquad (24)$$

Dilute Solution of a Strong Acid.

Since a strong monobasic acid in dilute solution is 100% ionised, the hydrogen-ion concentration is equal to the total molar concentration of acid.

$$[H^+] = [acid] \qquad . \qquad . \qquad . \quad (15)$$

$$pH = -\log [acid] \qquad . \qquad . \quad (16)$$

For example, 0·01M hydrochloric acid solution has a hydrogen-ion concentration of 10^{-2}; its pH is therefore $-\log (10^{-2}) = 2$.

Dilute Solution of a Weak Acid.

For a dilute solution of a weak monobasic acid HA containing no other electrolyte equation (10), p. 93, may be simplified as follows: The concentration of hydrogen ion produced by the water itself (10^{-7}) may be neglected, therefore $[H^+]$ is approximately equal to $[A^-]$. The degree of ionisation of the acid is slight, therefore the concentrations of undissociated HA molecules, $[HA]$, is approximately equal to the total concentration of acid. So equation (10) becomes

$$\frac{[H^+]^2}{[acid]} = K_a$$

or

$$[H^+] = \sqrt{K_a \cdot [acid]} \qquad . \qquad . \quad (17)$$

or by taking logarithms and changing signs

$$pH = \tfrac{1}{2} pK_a - \tfrac{1}{2} \log [acid] \qquad . \quad (18)$$

The pH of a 0·1M solution of lactic acid ($pK_a = 3·86$) is therefore

$$\tfrac{1}{2}[3·86] - \tfrac{1}{2} \log 0·1 = 1·93 + 0·50 = 2·43.$$

By methods similar to those used above for the hydrogen-ion concentrations of acids, the hydroxyl-ion concentrations of dilute solutions of strong and weak bases may be calculated. Thence the hydrogen-ion concentrations and pH values may be calculated; the results are as follows :

Dilute Solution of a Strong Base (e.g., *Sodium Hydroxide*).

$$[OH^-] = [base] \qquad . \qquad . \qquad . \qquad . \qquad . \quad (19)$$

$$[H^+] = \frac{K_w}{[base]}; \quad pH = 14 + \log [base] . \qquad . \qquad (20)$$

either a weak acid and a salt of that acid with a strong base (*e.g.*, acetic acid and sodium acetate) *or* a weak base and a salt of that base with a strong acid (*e.g.*, ammonium hydroxide and ammonium chloride).

pH of Solution containing a Weak Acid and its Salt with a Strong Base.

Equation (10), p. 93, can be applied to such a solution containing the acid HA and its salt Na+A−. Salts (with very few exceptions) are completely ionised. The dissociation of the weak acid HA, slight even in a solution containing no Na+A−, is depressed by A− ions of the salt (Common Ion Effect). The A− ion concentration of the buffer solution is therefore approximately equal to the concentration of salt in the solution, and [salt] may be written for [A−] in equation (10). The concentration of HA molecules in the solution is virtually equal to the concentration of acid in the solution, and [acid] may therefore be substituted for [HA] in equation (10). This equation then becomes

$$\frac{[H^+][\text{salt}]}{[\text{acid}]} = K_a$$

or

$$[H^+] = K_a\frac{[\text{acid}]}{[\text{salt}]} \qquad . \qquad . \qquad . \qquad (30)$$

Taking logarithms throughout, and changing signs,

$$pH = pK_a + \log\frac{[\text{salt}]}{[\text{acid}]} \qquad . \qquad . \qquad . \qquad (31)$$

This gives the *pH* of the buffer solution in terms of the *pK_a* of the acid and of the quantities of acid and salt (in g. mols. per litre) used to make up the solution.

The *pH* of a given buffer solution depends not on the absolute values of the concentrations of acid and salt, but on the *ratio* between these. The *pH* of such a solution is therefore *not* altered by dilution with water. (See experiment, p. 166.)

When a weak acid is 50% neutralised, *i.e.*, when [salt] = [acid], the *pH* of the solution is *equal* to the *pK_a* of the acid.

The resistance of a buffer solution to alteration of its *pH* on the addition of hydrogen ions is explained as follows. When a strong acid (*i.e.*, a quantity of hydrogen ions) is added to the buffer, the added hydrogen ions combine with A− ions of the salt, forming undissociated HA molecules:

$$H^+ + A^- \rightarrow HA.$$

Thus the concentration of *undissociated acid* molecules in the buffer *increases* and the concentration of *salt decreases* to the same extent.

Consider a buffer solution which is 1·00M in acetic acid and 1·00M in sodium acetate. The *pK_a* of acetic acid being 4·75, the *pH* of this

Strong-acid weak-base salts (e.g., ammonium chloride $NH_4^+Cl^-$) may be considered similarly. The weak-base cations combine with hydroxyl ions of the water, giving unionised base, while strong-acid anions do *not* combine with hydrogen ions. Thus the hydrogen-ion concentration of the solution is greater than its hydroxyl-ion concentration and the pH is *less than* 7.

$$NH_4^+ + Cl^- + H^+ + OH^- = NH_4OH + H^+ + Cl^-.$$

As above, the following equations may be derived :

$$[OH^-] = \sqrt{\frac{K_b.K_w}{[\text{salt}]}} \qquad . \qquad . \qquad . \qquad (25)$$

$$[H^+] = K_w \bigg/ \sqrt{\frac{K_b.K_w}{[\text{salt}]}} = \sqrt{\frac{K_w.[\text{salt}]}{K_b}} \qquad . \qquad (26)$$

$$pH = 7 - \tfrac{1}{2}pK_b - \tfrac{1}{2}\log[\text{salt}] \qquad . \qquad . \qquad . \qquad (27)$$

In a solution of a weak-acid weak-base salt (e.g., ammonium acetate) the anions of the salt combine with hydrogen ions and the cations of the salt combine with hydroxyl ions.

$$NH_4^+ + CH_3COO^- + H^+ + OH^- = CH_3.COOH + NH_4OH.$$

The relative extent to which these two processes take place—and hence the pH of the solution—depends on the relative strengths of acid and base. The following equations may be derived :

$$[H^+] = \sqrt{\frac{K_w.K_a}{K_b}} \qquad . \qquad . \qquad . \qquad . \qquad (28)$$

$$pH = 7 + \tfrac{1}{2}pK_a - \tfrac{1}{2}pK_b \qquad . \qquad . \qquad . \qquad (29)$$

For an experiment on the pH values of salt solutions see

6, 15   BUFFER SOLUTIONS

It has been pointed out () that most physiological processes take place only within a very narrow range of pH values. In many such processes acids or bases are produced. The processes would, therefore, stop themselves very quickly if the organism had no means of " mopping up " the hydrogen or hydroxyl ions formed. A solution which " mops up " hydrogen or hydroxyl ions, *i.e.*, resists changes in pH when an acid or base is added, is called a *buffer solution*. Living organisms are provided with many complex buffer systems.

Simple buffer solutions which are used in the laboratory contain

Consider an indicator HZ, which is a weak acid. Suppose that undissociated HZ molecules are *red*, and that Z⁻ ions are *yellow*.

$$HZ \; \rightleftharpoons \; H^{+} + Z^{-}$$
<div style="text-align:center">red   yellow</div>
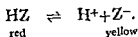
If the indicator is added to a solution of a strong acid (*e.g.*, hydrochloric acid), the large concentration of hydrogen ions present drives the equilibrium towards the left, in accordance with the Law of Mass Action.

$$HZ \; \leftarrow \; H^{+} + Z^{-}$$
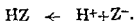
The indicator is therefore present almost entirely as unionised HZ molecules, and the solution is red.

Suppose that the indicator is added to a solution of a strong base (*e.g.*, sodium hydroxide). This solution contains a high concentration of hydroxyl ions and a low concentration of hydrogen ions. Here the dissociation reaction HZ → H⁺ + Z⁻ is favoured, the indicator is present mainly as Z⁻ ions, and the solution is therefore yellow.

In solutions of intermediate *pH*, some of the indicator is present as red HZ molecules and some as yellow Z⁻ ions ; the colour of the solution is therefore intermediate between red and yellow.

*p*K VALUES AND USEFUL RANGES OF INDICATORS

The dissociation of an indicator is considered quantitatively in the same way as the dissociation of any other weak acid or base. Each indicator has a dissociation constant K and a pK value. The buffer equation (31), p. 97, may be applied to solutions in which the indicator is partly neutralised, and provides a connection between the pH of the solution, the pK of the indicator, and the proportions of the indicator present as undissociated molecules and as ions.

For an indicator HZ, which is a weak acid,

$$pH \; = \; pK + \log\frac{[\text{salt}]}{[\text{acid}]} \; = \; pK + \log\frac{[Z^{-}]}{[HZ]} \qquad . \quad (33)$$

Since the colour of the solution is determined by the ratio $\frac{[Z^{-}]}{[HZ]}$, this equation shows that the colour depends on the pH of the solution and the pK of the indicator. When the indicator is half neutralised, the pH of the solution is *equal* to the pK of the indicator. The useful range of an indicator, *i.e.*, the pH range over which it changes *visibly* in colour, extends 0·5 to 1·0 pH units on each side of its half-neutralisation point.

Before an indicator can be used for determining pH values, a set of colour standards must be prepared. This is done by adding equal quantities of the indicator to equal volumes of a series of buffer solutions covering its useful range, the pH values of these buffers having previously been determined potentiometrically.

buffer will also be 4·75. Suppose that to 1000 ml. of this buffer 10 ml. 1·00M hydrochloric acid solution are added. Since hydrochloric acid is completely ionised, 0·01 g. ions of hydrogen ion have been added This 0·01 g. ions of hydrogen ion combines with 0·01 g. ions acetate ion, forming 0·01 g. mols. unionised acetic acid. The acetate ion concentration of the buffer will therefore have changed from 1·00 to 1·00−0·01=0·99. The acetic acid concentration will have changed from 1·00 to 1·00+0·01=1·01. The pH of the buffer is therefore now

$$4·75+\log \frac{0·99}{1·01}$$

$$=4·75-0·01$$

$$=4·74.$$

The change of 0·01 pH units is hardly detectable.

If 10 ml. 1·00M hydrochloric acid had been added to 1000 ml. pure water (pH=7), the resulting solution would have been 0·01M in hydrochloric acid, and its pH would have been 2, a change of 5 pH units.

The resistance of a buffer to alteration of its pH when an alkali is added may be treated similarly. Here the added hydroxyl ions interact with unionised HA molecules, giving A⁻ ions and water.

$$OH^-+HA \rightarrow A^-+HOH.$$

Thus the concentration of *salt* in the buffer *increases*, and the concentration of *undissociated acid* molecules *decreases* to the same extent.

An experiment illustrating the resistance of a buffer solution to changes in pH on the addition of acid and alkali is described on pp. 166–167.

pH of Solution containing a Weak Base and its Salt with a Strong Acid.

This type of buffer may be considered in a manner similar to that used for the weak-acid buffer above. The pH is given by the expression

$$pH = 14-\left\{ pK_b+\log \frac{[\text{salt}]}{[\text{base}]} \right\}. \qquad . \qquad . \qquad (32)$$

6, 16   ACID-BASE INDICATORS

Acid-base indicators are weak organic acids or bases, the ions of which (anions or cations respectively) differ in colour from the undissociated molecules from which they arise. They are used for the determination of pH values.
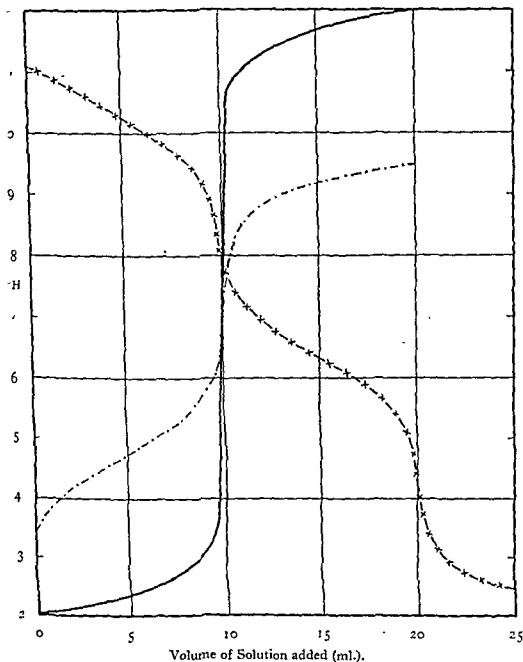
FIG. 6, 3

Titration Curves

Titrations carried out as described on p. 102.

———————— Strong-Base Strong-Acid NaOH added to HCl.

—·—·—·—·— Weak-Base Weak-Acid NH₄OH added to CH₃ COOH.

—x—x—x— Strong-Acid Carbonate HCl added to Na₂CO₃.

The vertical axis is labelled pH with values 2 through 11; the horizontal axis is labelled Volume of Solution added (ml.), with values 0, 5, 10, 15, 20, 25.

Indicators of different pK values covering the range from $pH=2$ to $pH=10$ are listed below. A mixture of indicators known as Universal Indicator is convenient for approximate pH determinations over the whole range (see p. 163).

For experiments on the use of indicators see pp. 162-167.

Indicator	pK	Colours and Useful pH Range
Methyl violet . . .	..	Yellow (fades) 0·0, green (fades) 1·0, blue 2·0, violet 3·0.
Thymol blue (first change)	1·7	Red 1·2- 2·8 yellow.
Bromophenol blue [1] . .	4·0	Yellow 3·0- 4·6 violet.
Bromocresol green . .	4·7	Yellow 3·8- 5·4 blue.
Methyl red . . .	5·1	Red 4·3- 6·1 yellow.
Bromocresol purple . .	6·3	Yellow 5·2- 6·8 purple.
Bromothymol blue [2] .	7·0	Yellow 6·0- 7·6 blue.
Phenol red . . .	7·9	Yellow 6·8- 8·4 red.
Thymol blue (second change)	8·9	Yellow 8·0- 9·6 blue.
Phenolphthalein . .	9·7	Colourless 8·2-10·0 pink.

6, 17   THE CHOICE OF INDICATORS IN ACID-BASE TITRATIONS

In a titration in which an acid HA interacts with a base BOH, the end-point required is the *point of chemical equivalence*, i.e., the point at which the substances HA and BOH have been mixed in the proportions required by the equation

$$HA + BOH = BA + HOH.$$

At this point the reaction-mixture is a solution of the salt BA.

The pH of the solution of a salt BA depends on the relative strengths of the acid HA and the base BOH from which the salt was formed (see pp. 95-96). It is equal to the pH of pure water (viz., 7) only if the acid and base are of equal strength ; only in this case is the titration carried to neutrality. Since acid-base indicators are simply means of determining pH values, the choice of indicator in a titration depends on the pH at the chemical equivalence-point (and hence on the strength of acid and base used).

Four general types of titration are considered here, followed by two special examples. The changes in pH of the reaction-mixture during

[1] Methyl orange ($pK=3·7$, useful range pH 3·1-4·4, red-yellow) is widely used, but is less satisfactory than bromophenol blue because its colour-change is less sharp.

[2] Litmus is a mixture of substances which changes colour from red to blue over the pH range 5-8. It is now used only for rough qualitative work.
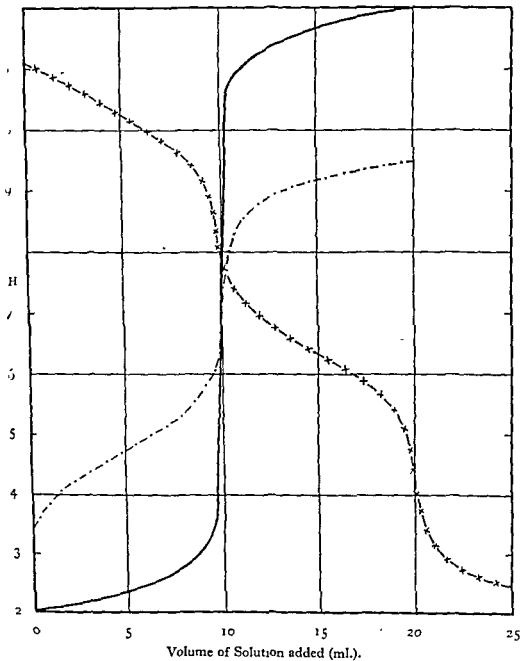
FIG. 6, 3

Titration Curves

Titrations carried out as described on p. 102.

———————— Strong-Base Strong-Acid NaOH added to HCl.

—·—·—·— Weak-Base Weak-Acid NH$_4$OH added to CH$_3$.COOH.

—x—x—x— Strong-Acid Carbonate HCl added to Na$_2$CO$_3$

the titrations are represented graphically, pH being plotted against volume of solution added. Figs. 6, 3 and 6, 4 show complete titration curves for the six titrations discussed below. Fig. 6, 5 is an enlargement of parts of the four principal curves, showing in more detail the changes in pH in the neighbourhood of the chemical equivalence-point.

In each titration 10·00 ml. of a 0·100M solution of one reagent were taken and diluted to 100 ml. Measured volumes of a 0·100M solution of the other reagent were then added to this from a burette with stirring, the pH of the mixture being determined potentiometrically after each addition.

The almost vertical sections of the curves represent large changes in pH for small additions from the burette. These sections correspond to chemical equivalence-points.

STRONG-BASE STRONG-ACID TITRATION

Example.—Sodium hydroxide, hydrochloric acid.

$$NaOH + HCl = NaCl + HOH.$$

Curve on Fig. 6, 3. Enlargement on Fig. 6, 5.

Here the pH at the chemical equivalence-point is 7·0. The pH changes so rapidly from 5 to 9 that any indicator whose colour change overlaps this range gives virtually the same result.

On account of the presence of carbonate in nearly all strong-base solutions, an indicator of low pK—e.g., bromophenol blue, $pK=4·0$, or methyl orange, $pK=3·7$—is generally used. See explanation under the description of a carbonate titration, pp. 107-108.

STRONG-BASE WEAK-ACID TITRATION

Example.—Sodium hydroxide, acetic acid.

$$NaOH + CH_3.COOH = CH_3.COONa + HOH.$$

Curve on Fig. 6, 4. Enlargement on Fig. 6, 5.

The pH at the chemical equivalence-point is *greater* than 7 on account of the hydrolysis of the salt, sodium acetate. The pK_a of acetic acid is 4·75, and the pH of 0·01M sodium acetate solution is 8·4.

An indicator, the useful range of which covers pH 8·4, is therefore wanted for this titration, and is provided by thymol blue (pH range 8·0-9·6) or phenolphthalein (pH range 8·2-10·0). Any indicator of lower pH range would change colour *before* the chemical equivalence-point was reached.

Note in Fig. 6, 4 the very gradual change in pH during the addition of alkali from 2 to 8 ml. This represents the *buffer range* of acetic acid sodium acetate mixtures.
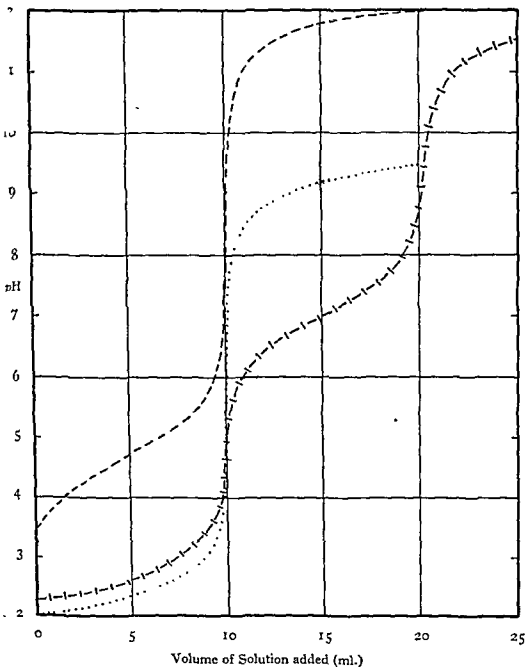
FIG. 6, 4

Titration Curves

Titrations carried out as described on p. 102.

– – – – – Strong-Base Weak-Acid   NaOH added to CH_3COOH.

·············· Weak-Base Strong-Acid NH_4OH added to HCl.

–·–·–·–·– Strong-Base Polybasic-Acid NaOH added to H_3PO_4.

For each stage the usual Mass Action equation relates the equilibrium concentrations of the ions and molecules concerned, and gives the dissociation constant for that stage. For orthophosphoric acid

$$\frac{[H^+][H_2PO_4^-]}{[H_3PO_4]} = K_1 ; \quad pK_1 = 2\cdot12$$

$$\frac{[H^+][HPO_4^{--}]}{[H_2PO_4^-]} = K_2 ; \quad pK_2 = 7\cdot21$$

$$\frac{[H^+][PO_4^{---}]}{[HPO_4^{--}]} = K_3 ; \quad pK_3 = 12\cdot30.$$

If the successive pK values of a polybasic acid differ by more than 4 units, it is possible with different indicators to distinguish the chemical equivalence-points at which one, two or more hydrogen atoms of the acid have been neutralised—i.e., the points at which the primary, secondary, etc., salts have been formed.

The titration curve of orthophosphoric acid with sodium hydroxide shows two sharp rises after the addition of one and two molecular proportions of sodium hydroxide, i.e., at the equivalence-points where the salts NaH_2PO_4 and Na_2HPO_4 have been formed. The pH values of the reaction-mixture at these two points are 5 and 9 respectively. Bromocresol green or methyl red will indicate the first, phenolphthalein or thymol blue the second equivalence-point.

There is no sharp rise in the titration curve at the third equivalence-point (addition of 30·0 ml. alkali; formation of Na_3PO_4). This point cannot therefore be determined by any indicator.

The portion of the titration curve from 12 to 18 ml. addition of alkali represents the *buffer range* of primary phosphate secondary phosphate mixtures.

For experiment, see p. 167.

STRONG-ACID CARBONATE TITRATION

Example.—Hydrochloric acid, sodium carbonate.

Curve on Fig. 6, 3.

Carbonic acid, H_2CO_3, is a weak dibasic acid ($pK_1=6\cdot37$, $pK_2=10\cdot25$). Solutions of its soluble salts have pH values higher than 7 due to hydrolysis.

When a solution of a carbonate is titrated with a strong acid the first sharp fall in pH comes when one equivalent of acid has been added, i.e., when the carbonate has been converted to bicarbonate,

$$Na_2CO_3+HCl = NaHCO_3+NaCl \quad \text{or} \quad CO_3^{--}+H^+ = HCO_3^-.$$
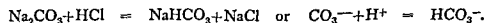
The pH is approximately 8 at this equivalence-point, which can be determined with phenolphthalein or thymol blue.

A second sharp fall in pH occurs when another equivalent of acid has been added, and the bicarbonate has been converted into carbonic acid or carbon dioxide and water.

$$NaHCO_3+HCl = H_2CO_3+NaCl \quad or \quad HCO_3^-+H^+ = H_2CO_3$$
$$(H_2CO_3 = CO_2 \uparrow +H_2O).$$
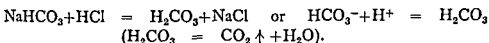
The pH is approximately 4·5 at this second equivalence-point, which can be determined with bromocresol green, bromophenol blue or, less satisfactorily, methyl orange.

The portion of the titration curve between 12 and 18 ml. addition of acid represents the *buffer range* of bicarbonate carbonic acid mixtures. This system is partly responsible for the buffering of blood.

If the reaction-mixture in a carbonate titration is boiled after each addition of acid, or if a current of carbon dioxide-free air is passed through it in the cold, bicarbonate is decomposed and carbon dioxide is evolved.

$$2NaHCO_3 = Na_2CO_3+CO_2 \uparrow +H_2O.$$
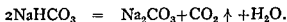
In this case the titration resembles the titration of sodium hydroxide with a strong acid, and all indicators with pK values between 9 and 5 give identical results, the colour change occurring after *two* equivalents of acid have been added.

$$Na_2CO_3+2HCl = 2NaCl+H_2O+CO_2.$$
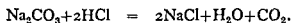
Effect of Carbonate on Titrations of Strong Bases

Unless solutions of strong bases are protected from atmospheric carbon dioxide they absorb it, forming carbonates. For example, two molecules of sodium hydroxide form one molecule of sodium carbonate thus:

$$2NaOH+CO_2 = Na_2CO_3+H_2O.$$

Suppose a sodium hydroxide solution which has become contaminated with carbonate is titrated with a strong acid to pH 7 (using bromothymol blue). At this point the sodium hydroxide has been transformed into chloride. The carbonate has been transformed into bicarbonate and chloride,

$$Na_2CO_3+HCl = NaHCO_3+NaCl,$$
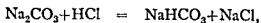
using only *half* as much acid as the sodium hydroxide from which it was formed would have used,

$$2NaOH+2HCl = 2NaCl+2H_2O.$$

Thus the more carbonate is formed, the lower is the acid titre of the alkali solution—so long as bromothymol blue is used as indicator.

If, however, the carbonate-contaminated alkali is titrated to pH 4·5 with bromocresol green, bromophenol blue or methyl orange as indicator, each molecule of sodium carbonate uses two equivalents of acid,

$$Na_2CO_3 + 2HCl = 2NaCl + CO_2 + H_2O,$$

and the titre of the alkali is the *same* as it was before the formation of any carbonate.

The same result can be obtained by boiling the carbonate-contaminated solution when it has been titrated to pH 7 with acid. This decomposes the bicarbonate and the pH of the solution rises above 7; the solution is then cooled and brought to pH 7 again by the addition of acid. The boiling, cooling and further addition of acid are repeated until no change in colour takes place on boiling, *i.e.*, until all carbonate has been decomposed.

6, 18   COMPETITION OF TWO ACIDS FOR ONE BASE

Many analytical reactions depend on the competition of two acids for one base.[1] The competition may be carried out by adding the two acids to the base, or by adding one acid to a salt of the other acid with the base. The outcome of such a competition depends on three factors:

1. the relative strengths of the acids;
2. the relative concentrations of the acids present;
3. the fairness or otherwise of the conditions in which the acids are allowed to react.

. . . .
. . . .
. . . .
if HA is added to BA′ it will *displace* HA′ from its salt,

$$HA + BA' \rightarrow HA' + BA.$$

Other factors being equal, the acid present in greater concentration will take a greater share of the base.

The third factor, fairness of competition, demands more consideration. Competition between the two acids is fair only if neither has a greater tendency to *escape* from the solution than the other. Escape . . . . -olatilisation, ... is sparingly

One or more of these " escape factors " may aid or may counteract the " relative strength factor." For experiment, see pp. 167-168.

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[1] Or of two bases for one acid. This problem, the converse of the one considered here, may be treated in the same way.

The following examples may be noted :

Case	Escape factor	Weaker acid	Stronger acid	Results
1		Volatile H_2S	Non-volatile H_2SO_4	$FeS+H_2SO_4$ $=FeSO_4+H_2S\uparrow$
2	Aids strength factor	Sparingly soluble benzoic acid	Soluble HCl	$C_6H_5COONa+HCl$ $=NaCl+C_6H_5COOH\downarrow$
3		Unstable H_2CO_3	Stable HCl	Na_2CO_3+2HCl $=H_2CO_3+2NaCl$; $H_2CO_3=CO_2\uparrow+H_2O$
4		Non-volatile H_3PO_4	Volatile HCl	H_3PO_4+NaCl $=NaH_2PO_4+HCl\uparrow$
5	Counteracts strength factor	Soluble	Sparingly soluble	No common example
6		Stable	Unstable	No common example

6, 19   THE DISSOLVING OF INSOLUBLE OR SPARINGLY SOLUBLE SUBSTANCES

Under this heading are described some reactions in which electrolytes, themselves insoluble or sparingly soluble in water, are somehow brought into aqueous solution by treatment with various reagents. It is wrong to say that the electrolytes are " soluble in " or " dissolved by " the reagents, since, as will be seen later, the insoluble electrolyte is in all cases transformed by the reagent into some other substance, which is soluble in water. The words " soluble " and " dissolved," *when used in this common but incorrect manner, are therefore put in inverted commas.* All these reactions depend upon interference by the reagent in the ionic equilibrium of the insoluble substance.

SOLUBILITY OF ACIDS IN ALKALIS

Many acids (chiefly organic acids), which are themselves sparingly soluble in water, form salts (commonly sodium or potassium salts) which are readily soluble in water. These acids can therefore be " dissolved " by sodium or potassium hydroxides. What really happens is that the sodium or potassium hydroxide reacts with the acid to form the sodium or potassium salt, which then dissolves in water.

Consider an acid HA (*e.g.*, benzoic acid, $C_6H_5.COOH$) which is sparingly soluble in water, but forms a sodium salt readily soluble in

If, however, the carbonate-contaminated alkali is titrated to pH 4·5 with bromocresol green, bromophenol blue or methyl orange as indicator, each molecule of sodium carbonate uses two equivalents of acid,

$$Na_2CO_3 + 2HCl \;=\; 2NaCl + CO_2 + H_2O,$$

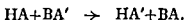and the titre of the alkali is the *same* as it was before the formation of any carbonate.

The same result can be obtained by boiling the carbonate-contaminated solution when it has been titrated to pH 7 with acid. This decomposes the bicarbonate and the pH of the solution rises above 7; the solution is then cooled and brought to pH 7 again by the addition of acid. The boiling, cooling and further addition of acid are repeated until no change in colour takes place on boiling, *i.e.*, until all carbonate has been decomposed.

6, 18   COMPETITION OF TWO ACIDS FOR ONE BASE

Many analytical reactions depend on the competition of two acids for one base.[1] The competition may be carried out by adding the *two acids to the base*, or by *adding one acid to a salt of the other acid with the base*. The outcome of such a competition depends on three factors :

1. the relative strengths of the acids ;
2. the relative concentrations of the acids present ;
3. the fairness or otherwise of the conditions in which the acids are allowed to react.

if HA is added to BA′ it will *displace* HA′ from its salt,
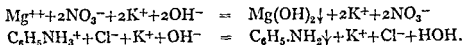
$$HA + BA' \;\rightarrow\; HA' + BA.$$

Other factors being equal, the acid present in greater concentration will take a greater share of the base.

The third factor, fairness of competition, demands more consideration. Competition between the two acids is fair only if neither has a greater tendency to *escape* from the solution than the other. Escape from the solution may take place in three ways, viz. : (*a*) volatilisation, if an acid has a low boiling-point, (*b*) precipitation, if an acid is sparingly soluble, (*c*) decomposition, if an acid is unstable.

One or more of these "escape factors" may aid or may counteract the "relative strength factor." For experiment, see pp. 167–168.

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[1] Or of two bases for one acid. This problem, the converse of the one considered here, may be treated in the same way.

" solutions " in acid by the addition of much hydroxyl ion (*i.e.*, by sodium or potassium hydroxide),

$$Mg^{++}+2NO_3^-+2K^++2OH^- \rightleftharpoons Mg(OH)_2\downarrow+2K^++2NO_3^-$$
$$C_6H_5NH_3^++Cl^-+K^++OH^- = C_6H_5.NH_2\downarrow+K^++Cl^-+HOH.$$

The transformation of a weak organic acid or base, which is sparingly soluble in water, into a highly-ionised salt, which is readily soluble in water, provides a very important means of separating an acidic or basic organic compound from water-insoluble compounds of neutral character. This is discussed further on p. 310.

SOLUBILITY OF SALTS IN ACIDS

Most weak-acid salts which are themselves insoluble in water may be " dissolved " by the strong mineral acids. Consider a salt B^+A^-, sparingly soluble in water, derived from a weak-acid HA. If solid B^+A^- is in contact with water, the following equilibrium is set up :

$$B^+A^- \rightleftharpoons B^++A^-.$$
$$\text{solid} \qquad \text{in solution}$$
$$\text{(trace)}$$
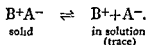
At equilibrium,

$$[B^+][A^-] = K_s.$$

Suppose hydrochloric acid (*i.e.*, a quantity of hydrogen ion) is added to the water. The acid HA being weak, some of the added hydrogen ions combine with some of the few A^- anions in solution. More solid B^+A^- dissolves to keep the solution saturated, and if 'sufficient strong acid is added, all the B^+A^- " dissolves."[1] The solution cannot properly be called a solution of B^+A^- in hydrochloric acid ; it is a solution containing the chloride of B^+ (dissociated) and the un-dissociated acid HA. The equation for the dissolving process should therefore be written

$$B^+A^-+H^++Cl^- = B^++Cl^-+HA.$$

The essential fact is that one ion of the sparingly soluble salt has been modified.

The " solubility " of many sparingly soluble salts, *e.g.*, carbonates, sulphides, sulphites, phosphates, in dilute hydrochloric acid may be explained thus. In the case of phosphates, the above ideas represent the whole process. If an attempt is made to bring the solution to neutrality, the insoluble phosphate is reprecipitated. For example, suppose calcium phosphate is " dissolved " in dilute hydrochloric acid, giving a solution of calcium chloride and phosphoric acid thus :

$$(Ca^{++})_3(PO_4^{---})_2+6H^++6Cl^- = 3Ca^{++}+6Cl^-+2H_3PO_4.$$
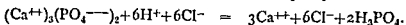
[1] It is presumed that B^+Cl^- *is* soluble in water, as are most chlorides. If B^+Cl^- is insoluble in water, another strong acid whose B salt is soluble in water is used.

water. When the acid is in contact with water the following equilibria are set up:

$$HA \rightleftharpoons HA \rightleftharpoons H^+ + A^-.$$
$$\text{solid} \qquad \text{in solution} \qquad \text{in solution}$$
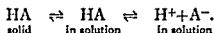
If a strong alkali (e.g., sodium hydroxide) is added to the solution, the hydroxyl-ion concentration is greatly increased and the hydrogen-ion concentration correspondingly diminished (since $[H^+][OH^-] = K_w$). The equilibria represented above are therefore disturbed, the reactions shown by arrows from left to right → being favoured. If sufficient alkali is added, the whole of the acid " dissolves," thus:

$$HA + Na^+ + OH^- = Na^+ + A^- + HOH.$$
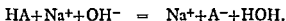
Sparingly soluble acids are reprecipitated from their " solutions " in alkali by the addition of much hydrogen ion—i.e., by strong acid,

$$Na^+ + A^- + H^+ + Cl = HA\downarrow + Na^+ + Cl^-.$$
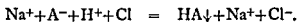
SOLUBILITY OF BASES IN ACIDS

Many bases (including most metallic hydroxides and many organic bases), which are themselves sparingly soluble or insoluble in water, form salts (commonly chlorides, nitrates or sulphates) which are readily soluble in water. These bases (and their anhydrides [1,2]) can therefore be " dissolved " by hydrochloric, nitric or sulphuric acids. What really happens is that the acid reacts with the base (or its anhydride) to form the chloride, nitrate or sulphate, which is soluble in water.

For example, magnesium hydroxide is sparingly soluble in water, but readily " soluble " in dilute nitric acid ; the product is a solution of magnesium nitrate.

$$Mg(OH)_2 + 2H^+ + 2NO_3^- = Mg^{++} + 2NO_3^- + 2HOH.$$

Aniline (phenylamine) is slightly soluble in water, giving the weak base phenylammonium hydroxide $C_6H_5.NH_3OH$.
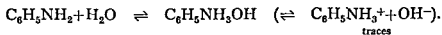
$$C_6H_5NH_2 + H_2O \rightleftharpoons C_6H_5NH_3OH \ (\rightleftharpoons C_6H_5NH_3^+ + OH^-).$$
$$\text{traces}$$

It is readily " soluble " in hydrochloric acid, giving a solution of aniline hydrochloride,

$$C_6H_5NH_3OH + H^+ + Cl^- = C_6H_5NH_3^+ + Cl^- + HOH.$$

Insoluble or sparingly soluble bases are reprecipitated from their

... ...oxides, e.g., the

..., RNH₃, are all

...nium hydroxides.

e.g., (RNH₃OH).

	Oxidation	Reduction
1A	*Increase* in the proportion of oxygen or other electro-negative constituent in a substance.	*Decrease* in the proportion of oxygen or other electro-negative constituent in a substance.
1B	*Decrease* in the proportion of hydrogen or other electro-positive constituent in a substance.	*Increase* in the proportion of hydrogen or other electro-positive constituent in a substance.
2	*Loss* of electrons by an atom, ion or molecule.	*Gain* of electrons by an atom, ion or molecule.

These different definitions of oxidation and reduction given above are not mutually exclusive, but are different ways of looking at the same thing; it is convenient to look at some reactions in one way and some in another.

Oxidation and reduction are complementary processes; an oxidation is always accompanied by a reduction, the *oxidising agent* being *reduced*, while the *reducing agent* is *oxidised*.

EQUIVALENTS AND EQUATIONS

The *gram-equivalent* of any substance acting as an *oxidising agent* is the weight of the substance which oxidises 1·008 g. of hydrogen, or which contains 8·000 g. of oxygen available for oxidising purposes, or which absorbs one Faraday or " gram-equivalent " of electrons in the reaction.

The *gram-equivalent* of any substance acting as a *reducing agent* is the weight of the substance which contains 1·008 g. of hydrogen available for reducing purposes, or which requires 8·000 g. of oxygen to oxidise it, or which gives up one Faraday of electrons in the reaction.

The equations for oxidation-reduction reactions are often complicated; they can be understood better if each is split into two "*half-equations*," one expressing the fate of the oxidising agent, the other that of the reducing agent.

In dealing with electrolytes the best method is to consider the oxidation-reduction reaction as a transfer of electrons. The "half-equations" then represent the processes which would take place at the electrodes if the reaction were used in a galvanic cell[1] as a source of current.

[1] If an oxidation-reduction reaction is made to generate a current in a galvanic cell, the electromotive force produced can be used as a quantitative measure of the reaction's tendency to take place, and of the *strength* of the oxidising and reducing agents concerned. For details see other books (*e.g.*, Vogel, *Quantitative Inorganic Analysis*, 1944, pp. 96–116).

If ammonium hydroxide is added to this solution (as in the precipitation of Group 3 in analysis) it reacts with the phosphoric acid giving ionised ammonium phosphate.

$$6NH_4OH + 2H_3PO_4 = 6NH_4^+ + 2PO_4^{---} + 6HOH.$$
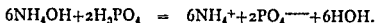
The two ions of the sparingly soluble calcium phosphate are now present in large concentrations, and the salt is reprecipitated.

Hence a special procedure (not described in this book) is necessary to deal with phosphates of Group 3 or 4 metals and of magnesium in qualitative analysis.

In the case of sulphides (*e.g.*, ferrous sulphide) the acid is volatile and, if the solution is boiled, escapes from it.

$$FeS + 2H^+ + 2Cl^- = Fe^{++} + 2Cl^- + H_2S\uparrow.$$
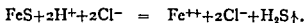
The solution then contains only the strong-acid salt, and no precipitation occurs if the solution is neutralised. In the case of carbonates and sulphites the corresponding acids are not volatile, but are unstable, giving rise to volatile decomposition products. Thus with calcium carbonate,

$$CaCO_3 + 2H^+ + 2Cl^- = Ca^{++} + 2Cl^- + H_2CO_3 ;$$
$$H_2CO_3 = CO_2\uparrow + H_2O.$$
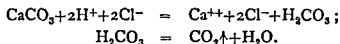
On warming the solution, the decomposition products of the weak acid are eliminated, and the strong-acid salt remains. Again, the final solution may be neutralised without precipitation occurring.
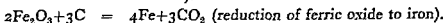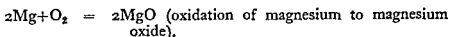
STRONG-ACID SALTS

Sparingly soluble salts of strong acids, *e.g.*, silver chloride, *cannot* be brought into solution by treatment with other strong acids, since here the anion of the sparingly soluble salt (Cl^-) will *not* combine with added hydrogen ion.

OTHER MATTERS

6, 20   OXIDATION AND REDUCTION

Oxidation and reduction were originally defined respectively as gain and loss of oxygen by a substance, *e.g.*,

$$2Mg + O_2 = 2MgO \text{ (oxidation of magnesium to magnesium oxide).}$$

$$2Fe_2O_3 + 3C = 4Fe + 3CO_2 \text{ (reduction of ferric oxide to iron).}$$

Oxidation and reduction are now more generally defined in the following ways, *either* (definitions 1A and 1B) in terms of changes in the proportions of different elements present, *or* (definition 2) in terms of a transfer of electrons.

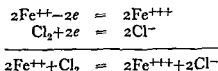### 3. The Oxidation of a Ferrous to a Ferric Salt by Chlorine.

" *Atomic* " *Treatment.*

The ferrous salt (*e.g.*, chloride) combines with chlorine to form ferric salt ; since the proportion of electronegative constituent in the compound increases, the ferrous salt is oxidised. The chlorine is reduced, since it becomes part of a compound containing an electro-positive constituent (iron).

$$2FeCl_2 + Cl_2 = 2FeCl_3.$$
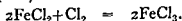
" *Electronic* " *Treatment.*

The ferrous ions yield electrons to the chlorine. The ferrous ions are thus oxidised to ferric ions ; the chlorine molecules are reduced to chloride ions.

$$2Fe^{++} - 2e = 2Fe^{+++}$$
$$Cl_2 + 2e = 2Cl^-$$
$$\overline{\phantom{2Fe^{++} + Cl_2 = 2Fe^{+++} + 2Cl^-}}$$
$$2Fe^{++} + Cl_2 = 2Fe^{+++} + 2Cl^-$$

4. The Reaction between Iodine and Thiosulphate.

" *Electronic* " *Treatment.*

Iodine oxidises thiosulphate ($S_2O_3^{--}$) ions in solution to tetra-thionate ($S_4O_6^{--}$) ions, being itself reduced to iodide (I^-) ions.

The oxidation of thiosulphate to tetrathionate ions consists in the removal of two electrons from two thiosulphate ions, which then combine to give one tetrathionate ion. The " half-equation " is

$$2S_2O_3^{--} - 2e = S_4O_6^{--} \qquad . \qquad . \qquad . \qquad . \qquad (A)$$

The reduction of iodine to iodide consists in the addition of two electrons to one molecule of iodine forming two iodide ions. The " half-equation " is

$$I_2 + 2e = 2I^- \qquad . \qquad . \qquad . \qquad . \qquad . \qquad (B)$$

The equation for the reaction between thiosulphates and iodine is obtained by adding the " half-equations " (A) and (B), and is

$$2S_2O_3^{--} + I_2 = S_4O_6^{--} + 2I^- \qquad . \qquad . \qquad . \qquad (C)$$

From equations (A) and (B) and the definitions above, it is seen that the gram-equivalents of sodium thiosulphate and iodine *in this reaction* are the gram-molecular weight and the gram-atomic weight respectively.

5. The Reaction between Permanganates and Ferrous Salts.

" *Electronic* " *Treatment.*

Permanganate ions (MnO_4^-) in acid solution oxidise ferrous ions (Fe^{++}) to ferric ions (Fe^{+++}), being themselves reduced to manganous ions (Mn^{++}).

In dealing with non-electrolytes it is often more convenient to consider the oxidation-reduction reaction as gain and loss of oxygen, hydrogen, etc. This treatment may sometimes be found convenient for the more complicated oxidation-reduction reactions of electrolytes (see example 5, p. 116). *It is, however, open to the objection that the " half-equations " used are purely imaginary, and nothing more than an aid to memory.* In this treatment the oxidising agent is considered as splitting up into " oxidising oxygen "—written (O)—and a residue, while the reducing agent is considered as taking up the " oxidising oxygen." Alternatively the reducing agent is considered as splitting up into " reducing hydrogen "—written (H)—and a residue, while the oxidising agent takes up the " reducing hydrogen."

EXAMPLES

The following examples illustrate these methods of treatment, which may be called " atomic " and " electronic ":

### 1. The Solution of a Metal in an Acid.

" *Atomic* " *Treatment.*

The metal (*e.g.*, zinc) is oxidised to its salt, *e.g.*, zinc chloride (containing the electronegative constituent chlorine), while hydrogen gas (containing no electronegative constituent) is liberated.

$$Zn + 2HCl = ZnCl_2 + H_2\uparrow.$$
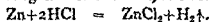
" *Electronic* " *Treatment.*

The metal atoms lose electrons, forming cations, and are oxidised. The hydrogen ions of the acid gain electrons, forming hydrogen atoms (which then combine to form molecules), and are reduced.
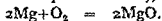
The symbol " *e* " is used to represent one Faraday of electrons.

$$\begin{aligned} Zn - 2e &= Zn^{++} \\ 2H^+ + 2e &= H_2 \\ \hline Zn + 2H^+ &= Zn^{++} + H_2\uparrow \end{aligned}$$
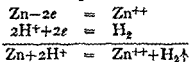
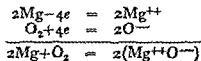### 2. The Burning of a Metal in Oxygen.

" *Atomic* " *Treatment.*

The metal (*e.g.*, magnesium) is oxidised to its oxide (containing the electronegative constituent oxygen); the oxygen is reduced to the oxide (containing the electropositive metal).
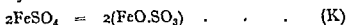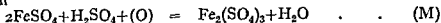
$$2Mg + O_2 = 2MgO.$$

" *Electronic* " *Treatment.*

The metal, which is oxidised, yields electrons to the oxygen, which is reduced.

$$\begin{aligned} 2Mg - 4e &= 2Mg^{++} \\ O_2 + 4e &= 2O^{--} \\ \hline 2Mg + O_2 &= 2(Mg^{++}O^{--}) \end{aligned}$$

The essential reaction on the part of the ferrous sulphate is the absorption of oxygen by FeO.

$$2FeSO_4 = 2(FeO.SO_3) \quad . \quad . \quad . \quad (K)$$

$$2FeO+(O) = Fe_2O_3 \quad . \quad . \quad . \quad (L)$$

The " half-equation " for the fate of the ferrous sulphate can be written

$$2FeSO_4+H_2SO_4+(O) = Fe_2(SO_4)_3+H_2O \quad . \quad . \quad (M)$$

Multiplying equation (M) by five and adding equation (J), we get the complete equation (N):

$$2KMnO_4+10FeSO_4+8H_2SO_4$$
$$= K_2SO_4+2MnSO_4+5Fe_2(SO_4)_3+8H_2O \quad (N)$$

Equation (N), unlike all the preceding partial equations, is a statement of a physical reality. It would, however, be foolish to try to remember this equation itself. If equations (H) and (L), which contain the essence of the process, are remembered, the full equation can be built up from these.

From " half-equation " (J) above it is seen that two gram-molecules of potassium permanganate yield in this reaction five gram-atoms (i.e., 80·00 g.) of available oxygen. Therefore one-fifth of a gram-molecule of potassium permanganate yields 8·000 g. available oxygen, and the gram-equivalent of potassium permanganate in this reaction is one-fifth of its gram-molecular weight.

Similarly from " half-equation " (M) it is seen that two gram-molecules of ferrous sulphate absorb one gram-atom (i.e., 16·00 g.) of available oxygen. Therefore one gram-molecule of ferrous sulphate absorbs 8·000 g. available oxygen, and the gram-equivalent of ferrous sulphate in this reaction is the same as its gram-molecular weight.

6. Oxidation of an Aldehyde to a Carboxylic Acid.

Aldehydes (general formula R.CHO) are oxidised to carboxylic acids (general formula R.COOH) by many oxidising agents, among them ammoniacal silver nitrate, which is virtually a solution of silver oxide (" Ag_2O "). This reagent is reduced to silver metal.
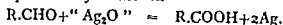
" Atomic " Treatment.

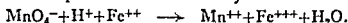The oxidising agent, ammoniacal silver nitrate, provides oxygen thus :   " Ag_2O " $= 2Ag+(O)$.

This oxidising oxygen (O) is absorbed by the aldehyde.

$$R.CHO+(O) = R.COOH.$$

The complete equation may be written

$$R.CHO+" Ag_2O " = R.COOH+2Ag.$$

The reactants and products are indicated by the skeleton expression

$$MnO_4^- + H^+ + Fe^{++} \longrightarrow Mn^{++} + Fe^{+++} + H_2O.$$

The " half-equation " for the fate of the reducing agent (ferrous ions) is easily written thus :

$$Fe^{++} - e = Fe^{+++} \qquad . \qquad . \qquad (D)$$

The " half-equation " for the fate of the oxidising agent (permanganate ions) can be deduced as follows. The skeleton of the equation is

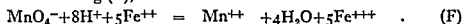$$MnO_4^- + H^+ \longrightarrow Mn^{++} + H_2O.$$

To balance the numbers of atoms this must be written

$$MnO_4^- + 8H^+ \longrightarrow Mn^{++} + 4H_2O.$$

To balance the electric charges five Faradays of electrons (provided by the reducing agent) must be added to the left-hand side ; the " half-equation " is then

$$MnO_4^- + 8H^+ + 5e = Mn^{++} + 4H_2O \qquad . \qquad . \qquad (E)$$

The equation for the whole reaction, obtained by multiplying (D) by five and adding (E), is

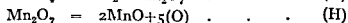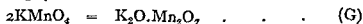$$MnO_4^- + 8H^+ + 5Fe^{++} = Mn^{++} + 4H_2O + 5Fe^{+++} \qquad . \qquad (F)$$

From equation (D) it is seen that the gram-equivalent of ferrous sulphate *in this reaction* is the weight containing one gram-atom of iron. From equation (E) it is seen that, since one gram-ion of permanganate absorbs *five* Faradays of electrons, the gram-equivalent of potassium permanganate *in this reaction* must be *one-fifth* of its gram-molecular weight.
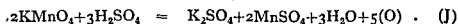
" Atomic " Treatment.

In this treatment the formulæ of oxy-acid salts are conveniently written in the two-oxide form, *e.g.*, $FeO.SO_3$ for $FeSO_4$, $K_2O.Mn_2O_7$ for $2KMnO_4$, since as a rule only one of the two parts of the salt undergoes oxidation or reduction.
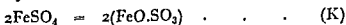
Consider as an example the oxidation of ferrous sulphate by potassium permanganate in the presence of dilute sulphuric acid. The essential reaction on the part of the permanganate is the provision of oxygen by the Mn_2O_7.

$$2KMnO_4 = K_2O.Mn_2O_7 \qquad . \qquad . \qquad . \qquad (G)$$

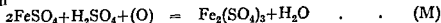$$Mn_2O_7 = 2MnO + 5(O) \qquad . \qquad . \qquad . \qquad (H)$$

Since sulphuric acid is present, the actual products are potassium and manganous sulphates, and we can write the following " half-equation " for the fate of the permanganate :
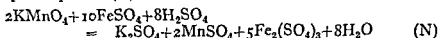
$$2KMnO_4 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 3H_2O + 5(O) \qquad . \qquad (J)$$

The essential reaction on the part of the ferrous sulphate is the absorption of oxygen by FeO.

$$2FeSO_4 = 2(FeO.SO_3) \qquad . \qquad . \qquad . \qquad (K)$$

$$2FeO+(O) = Fe_2O_3 \qquad . \qquad . \qquad . \qquad (L)$$

The "half-equation" for the fate of the ferrous sulphate can be written

$$2FeSO_4+H_2SO_4+(O) = Fe_2(SO_4)_3+H_2O \qquad . \qquad (M)$$

Multiplying equation (M) by five and adding equation (J), we get the complete equation (N):

$$2KMnO_4+10FeSO_4+8H_2SO_4$$
$$= K_2SO_4+2MnSO_4+5Fe_2(SO_4)_3+8H_2O \qquad (N)$$

Equation (N), unlike all the preceding partial equations, is a statement of a physical reality. It would, however, be foolish to try to remember this equation itself. If equations (H) and (L), which contain the essence of the process, are remembered, the full equation can be built up from these.

From "half-equation" (J) above it is seen that two gram-molecules of potassium permanganate yield in this reaction five gram-atoms (*i.e.*, 80·00 g.) of available oxygen. Therefore one-fifth of a gram-molecule of potassium permanganate yields 8·000 g. available oxygen, and the gram-equivalent of potassium permanganate *in this reaction* is one-fifth of its gram-molecular weight.

Similarly from "half-equation" (M) it is seen that two gram-molecules of ferrous sulphate absorb one gram-atom (*i.e.*, 16·00 g.) of available oxygen. Therefore one gram-molecule of ferrous sulphate absorbs 8·000 g. available oxygen, and the gram-equivalent of ferrous sulphate *in this reaction* is the same as its gram-molecular weight.
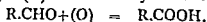
6. Oxidation of an Aldehyde to a Carboxylic Acid.

Aldehydes (general formula R.CHO) are oxidised to carboxylic acids (general formula R.COOH) by many oxidising agents, among them ammoniacal silver nitrate, which is virtually a solution of silver oxide (" Ag$_2$O "). This reagent is reduced to silver metal.

" *Atomic* " *Treatment.*

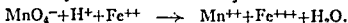The oxidising agent, ammoniacal silver nitrate, provides oxygen thus :

$$\text{`` Ag}_2\text{O ''} = 2Ag+(O).$$

This oxidising oxygen (O) is absorbed by the aldehyde.

$$R.CHO+(O) = R.COOH.$$

The complete equation may be written

$$R.CHO+\text{`` Ag}_2\text{O ''} = R.COOH+2Ag.$$

The reactants and products are indicated by the skeleton expression

$$MnO_4^- + H^+ + Fe^{++} \longrightarrow Mn^{++} + Fe^{+++} + H_2O.$$

The "half-equation" for the fate of the reducing agent (ferrous ions) is easily written thus:

$$Fe^{++} - e = Fe^{+++} \quad . \quad . \quad . \quad (D)$$

The "half-equation" for the fate of the oxidising agent (permanganate ions) can be deduced as follows. The skeleton of the equation is

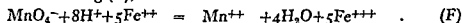$$MnO_4^- + H^+ \longrightarrow Mn^{++} + H_2O.$$

To balance the numbers of atoms this must be written

$$MnO_4^- + 8H^+ \longrightarrow Mn^{++} + 4H_2O.$$

To balance the electric charges five Faradays of electrons (provided by the reducing agent) must be added to the left-hand side; the "half-equation" is then

$$MnO_4^- + 8H^+ + 5e = Mn^{++} + 4H_2O \quad . \quad . \quad (E)$$

The equation for the whole reaction, obtained by multiplying (D) by five and adding (E), is

$$MnO_4^- + 8H^+ + 5Fe^{++} = Mn^{++} + 4H_2O + 5Fe^{+++} \quad . \quad (F)$$
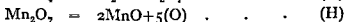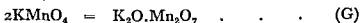
From equation (D) it is seen that the gram-equivalent of ferrous sulphate *in this reaction* is the weight containing one gram-atom of iron. From equation (E) it is seen that, since one gram-ion of permanganate absorbs *five* Faradays of electrons, the gram-equivalent of potassium permanganate *in this reaction* must be *one-fifth* of its gram-molecular weight.

"Atomic" Treatment.

In this treatment the formulæ of oxy-acid salts are conveniently written in the two-oxide form, *e.g.*, $FeO.SO_3$ for $FeSO_4$, $K_2O.Mn_2O_7$ for $2KMnO_4$, since as a rule only one of the two parts of the salt undergoes oxidation or reduction.

Consider as an example the oxidation of ferrous sulphate by potassium permanganate in the presence of dilute sulphuric acid. The essential reaction on the part of the permanganate is the provision of oxygen by the Mn_2O_7.

$$2KMnO_4 = K_2O.Mn_2O_7 \quad . \quad . \quad . \quad (G)$$
$$Mn_2O_7 = 2MnO + 5(O) \quad . \quad . \quad . \quad (H)$$

Since sulphuric acid is present, the actual products are potassium and manganous sulphates, and we can write the following "half-equation" for the fate of the permanganate:

$$2KMnO_4 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 3H_2O + 5(O) \quad . \quad (J)$$

For electrolytes, P, V and T are related by the equation

$$PV = iRT$$

where i is the ratio,

$$\frac{\text{total number of solute particles (molecules+ions)}}{\substack{\text{number of solute particles which would} \\ \text{be present if there were no dissociation}}}$$

For an electrolyte which produces 2 ions per molecule (*e.g.*, sodium chloride) and is 100% dissociated, $i=2\cdot0$.

The surface membranes of most living cells are semi-permeable, and osmotic phenomena play an important part in the exchanges between cells and their aqueous environment.

It is impossible to arrange a simple experiment on osmotic pressure for elementary classes, since it is very difficult to provide good semi-permeable membranes.

6, 22   DEPRESSION OF THE FREEZING-POINT

The freezing-point of a liquid is lowered by a solute.   For example, water freezes at $0\cdot00°$; a solution of 180 g. glucose in 1000 g. water freezes at $-1\cdot86$. The depression of the freezing-point (D) of a given solvent by all non-electrolyte solutes is proportional to the molar concentration (C) of the solute.

$D=K.C$, where K is a constant [1] for the solvent, called the *molecular depression constant*.

In solutions of electrolytes each solute ion has the same effect on the freezing-point as a solute molecule. Here $D=i.K.C$, where i has the same meaning as in the osmotic pressure equation given above.

An experiment showing the depression of the freezing-point of water by equimolecular concentrations of a non-electrolyte and an electrolyte is described on pp. 168–169.

Great use is made of the principle of freezing-point depression in testing the purity and the identity of substances in organic chemistry.

MELTING-POINTS OF PURE SUBSTANCES AND MIXTURES

A *pure substance* melts [2] completely at one temperature, *i.e.*, the melting-point is *sharp*.

A *substance containing impurities* melts at a temperature lower than the melting-point of the pure substance, and usually over a range of temperature, *i.e.*, the melting-point is *depressed* by the impurities and

---

[1] The theoretical connection which exists between the osmotic pressure, the lowering of vapour pressure and depression of the freezing-point of a solution is not discussed here.

[2] Substances which decompose at or below their melting-points are disregarded here.

### 7. Reduction of a Nitro Compound to an Amine.

Aromatic nitro compounds ($Ar.NO_2$) are reduced by nascent hydrogen—*i.e.*, hydrogen made on the spot (in this case from a metal and acid)—to primary aromatic amines ($Ar.NH_2$).
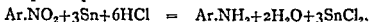
" Atomic " Treatment.

Nascent hydrogen is provided by tin and hydrochloric acid thus:

$$3Sn+6HCl = 6(H)+3SnCl_2.$$

This nascent hydrogen then reacts with the nitro compound.

$$Ar.NO_2+6(H) = Ar.NH_2+2H_2O.$$
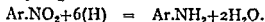
The complete equation for the reaction is

$$Ar.NO_2+3Sn+6HCl = Ar.NH_2+2H_2O+3SnCl_2.$$

6, 21   OSMOTIC PRESSURE

The osmotic pressure of a solution is a measure of the solution's tendency to dilute itself with solvent. This tendency may be demonstrated by means of a membrane, permeable to solvent but not to solute molecules, which is called a *semipermeable membrane*. If a solution is separated from its solvent by a semipermeable membrane, solvent will flow through the membrane towards the solution. The osmotic pressure of a solution may be measured by determining the pressure which, when applied to the solution, just prevents the influx of solvent through the membrane. If two solutions of different concentrations (A and B) are separated by a semipermeable membrane, solvent will flow through the membrane from the less to the more concentrated solution. If solutions A and B have equal osmotic pressure they are said to be *isotonic*; if the osmotic pressure of A is greater than that of B, A is said to be *hypertonic* with respect to B, and B *hypotonic* with respect to A.

For all solutions of non-electrolytes the relation between the osmotic pressure P, the volume in litres V containing 1 gram-molecule of solute and the absolute temperature T is given by the equation

$$PV = RT$$

where R is a constant, numerically equal to the constant in the general gas equation. Thus at constant temperature $P \propto \dfrac{1}{V}$ or $P \propto$ concentration of solute.

In solutions of electrolytes each ion has the same osmotic effect as an undissociated molecule. A solution of an electrolyte, therefore, has a *greater* osmotic pressure than a non-electrolyte solution of the same molar concentration.

6, 23

SURFACE CHEMISTRY

ADSORPTION

The importance of surfaces as the only places where interaction between immiscible substances can take place has already been emphasised (pp. 74-75). In many cases substances which might be expected to distribute themselves evenly throughout a phase are found to be concentrated at a surface. Thus solutes may concentrate themselves at the surface between the solution and a solid. If, for example, an aqueous solution of acetic acid is shaken with finely divided charcoal, much of the acid is adsorbed on the surface of the charcoal, and the concentration of acid in the bulk of the solution is greatly reduced (see experiment, pp. 169-170).

This adsorption at the surface is due to different forces in different examples. In some cases, the forces are ionic; e.g., proteins, whose molecules may be considered as very large anions or cations, adsorb ions of the opposite charge (presumably by direct ionic combination). If the adsorbed ions are coloured, the proteins are stained (see experiment, pp. 404-405). The forces causing adsorption of acetic acid on charcoal are probably not ionic, but are nevertheless quite strong.

DIFFERENTIAL ADSORPTION

Substances differ in the force with which they are adsorbed. Acetone, for example, is more strongly adsorbed by charcoal than is acetic acid. If charcoal which has adsorbed acetic acid is subsequently treated with acetone, the latter displaces the acid from the charcoal.

Differential adsorption of solutes has many important applications. The use of charcoal for removing coloured impurities from colourless organic compounds during crystallisation depends on the preferential adsorption of the impurities, which are often substances of higher molecular weight than the desired product. The chromatographic method, which effects many otherwise difficult separations, depends on differential adsorption of organic compounds on a column of finely powdered solid (often aluminium oxide)

CATALYSIS AT SURFACES

Many gaseous reactions are catalysed by finely divided metals (e.g., platinum); the gases are adsorbed on the surface of the metal and react there. (An example is the combination of sulphur dioxide and oxygen when passed over platinised asbestos.)

The biological catalysts called *enzymes* probably act in a similar way. Enzymes are organic compounds of high molecular weight (all so far known are of protein character), which catalyse various changes in simpler compounds (*substrates*) which are adsorbed from aqueous solution on their surfaces. Competition between two substrates for a place on the surface of an enzyme is of great biological importance.

is usually *not sharp*. For example, pure benzoic acid melts sharply at
122°; a sample of benzoic acid mixed with 10% by weight of urea
melts over the range 85-90°.

When it is necessary to purify a solid it must be repeatedly re-
crystallised, or treated in any other way which might remove impurities,
until further treatment does *not* raise or sharpen the melting-point.

The Mixed Melting-point Method of Determining Identities.

If two fusible compounds are mixed, each behaves as an impurity
with regard to the other, and as a rule lowers its melting-point.[1] This
is true even if the two compounds when pure have almost identical
melting-points. The following example is particularly impressive,
since the two compounds are of the same chemical type :

Benzidine $H_2N.C_6H_4.C_6H_4.NH_2$.   .   .   m.p. 127-128

o-Tolidine (dimethylbenzidine)
   $H_2N.C_6H_3(CH_3).C_6H_3(CH_3).NH_2$.   .   m.p. 128-129

Mixture of equal parts by weight of benzidine and
   o-tolidine   .   .   .   .   .   m.p. 95-105

The identity of two samples which have the same melting-point and
the same chemical properties may be tested by determining the melting-
point of a mixture of the samples.

Suppose a compound X is to be identified ; its chemical properties
indicate that it is an aromatic amine of the benzidine type ; its melting-
point is 127-128°. Reference to tables suggests that this compound
may be benzidine (A) or *o*-tolidine (B). Authentic specimens of A and
B are obtained, and the melting-points of the following mixtures
determined,

    (1) a mixture of equal parts X and A,
    (2)   ,,   ,,   ,,   X and B.

Then if the melting-point of (1) is 127-128° and that of (2) is below
127°, X=A. Conversely, if the melting-point of (2) is 127-128° and
the melting-point of (1) is below 127°, X=B.

The following pairs of substances, although not of the same chemical
type, are suitable for demonstrating the mixed melting-point method
to students :

			m.p.
Acetanilide	$C_6H_5.NH.CO.CH_3$.	. . .	114°
Fluorene	$C_{13}H_{10}$.	. . .	116°
Cinnamic acid	$C_6H_5.CH:CH.COOH$	. . .	133°
Urea	$CO(NH_2)_2$	. . .	133°

Details of methods for determining melting-points are given on
pp. 65-68.

    [1] There are a few exceptions to this rule.

6, 24 COLLOIDAL SOLUTIONS

Colloidal solutions are heterogeneous systems, which differ from suspensions and from true solutions in the *size* of the *particles* of the dispersed substance which are present.

The continuous phase in a colloidal solution, which corresponds to the solvent in a true solution, is called the *dispersion medium*; the particles, which correspond to the solute in a true solution, are called the *disperse phase*.

The approximate ranges of particle-size, and some differences in properties dependent on these, are as follows:

	True Solutions	Colloidal Solutions	Suspensions
Particle size	< 1 mµ	1–100 mµ	> 100 mµ
Visibility of particles.	Particles *not* shown by microscope or by other optical effects.	Particles *not* visible under microscope; presence shown by certain optical effects.	Particles visible under microscope.
Penetrating power of particles.	Pass readily through filter-paper or dialysing membrane and into gel.	Pass through filter-paper; do *not* pass through dialysing membrane or into gel.	Do *not* pass through filter-paper or dialysing membrane or into gel.

Substances of high molecular weight such as proteins and polysaccharides, if they can be dispersed in liquids at all, form colloidal and not true solutions. Since all living cells contain substances in colloidal solution, the behaviour of such materials is of very great importance to the student of medicine or biology.

Two experiments on the size of particles in suspension, colloidal solution and true solution, are described on pp. 170–171. Experiments on the ultramicroscope and the Tyndall effect are suitable for demonstrations, but not for class work.

TYPES OF COLLOIDAL SOLUTIONS

Disperse phase and dispersion medium may each be solid, liquid or gaseous. The most important colloidal solutions are dispersions of solids or liquids in liquids (*sols*) and related systems, called *gels*. Except for the last paragraph, the rest of this section is concerned only with sols. Examples of sols are the colloidal solutions of proteins, starch, glycogen, arsenious sulphide and ferric hydroxide in water; examples of gels are those formed by high concentrations of proteins or starch in water.

EMULSIFICATION

The adsorption of certain substances at the interface between two immiscible liquids is of great importance in promoting the dispersion of fine drops of one liquid in the other (emulsification). In all important examples, one of the two immiscible liquids is water, the other is an organic compound immiscible with it, e.g., an ester of high molecular weight, such as triolein (see pp. 375-376).
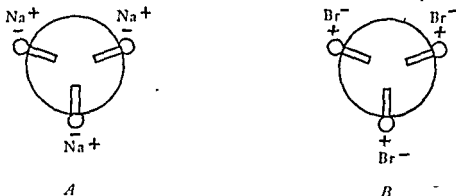

Fig. 6, 6

Behaviour of Emulsifying Agents

The two large circles represent oil-drops in aqueous media. The symbols ⊂⊐ and ⊂⊐+ represent the ions of emulsifying agents, the straight portions representing the oil-soluble hydrocarbon radicals and the small circles the water-soluble ionised radicals (carboxylate in A, quaternary ammonium in B).

Emulsifying agents are substances whose molecules are composed of two parts, one of which tends to dissolve in one of the two immiscible liquids, while the other tends to dissolve in the other liquid. For emulsifying oils for water, the agent must have a water-attractive radical, e.g., carboxyl-COOH, or preferably the highly ionised carboxylate anion radical-COO⁻M⁺, and an oil-soluble radical, e.g., a long hydrocarbon chain. Long-chain fatty acids, e.g., oleic acid
C̲ ̲H̲ ̲COOH̲ ̲ ̲ ̲ ̲ ̲ ̲ ̲ ̲s̲o̲d̲i̲u̲m̲ ̲o̲l̲e̲a̲t̲e̲ ̲C̲ ̲H̲ ̲COO-Na̲+̲ ̲therefore

emulsifying agents, e.g., salts of certain conjugated acids present in bile (which emulsify fats in the duodenum and so help their digestion), and long-chain quaternary ammonium salts $R_4N^+Hal^-$, the so-called "invert soaps" such as cetyltrimethylammonium bromide $C_{16}H_{33}.N(CH_3)_3^+Br^-$. Fig. 6, 6 illustrates the way in which the molecules of the emulsifying agent arrange themselves, each of the two parts placing itself in the liquid in which it is soluble. (For experiment see p. 170.)

Examples of the different types of sol are as follows :

Lyophobic sols (particles positively charged) : ferric hydroxide, aluminium hydroxide.

Lyophobic sols (particles negatively charged) : arsenious sulphide, gold.

Lyophilic sols : proteins, starch, glycogen.

The particles and the mechanisms of coagulation may be represented very crudely thus :

1. *Lyophobic Sol.*

$$\boxed{\begin{array}{c} As_2S_3 \\ S^{--} \end{array}} \quad 2H^+$$
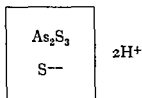
The arsenious sulphide particles have adsorbed sulphide ions and therefore carry negative charges ; they repel each other. Positive ions are present in the solution.

If an electrolyte B^+A^- is added to the colloidal solution, B^+ ions are also adsorbed on the particles, which become electrically neutral and no longer repel one another. On collision they coalesce and the sol is precipitated.

$$\boxed{\begin{array}{c} As_2S_3 \\ S^{--} \end{array}} \quad 2H^+ + 2B^+ + 2A^- \quad \longrightarrow \quad \boxed{\begin{array}{c} As_2S_3 \\ 2B + S^{--} \end{array}} \quad + 2H^+ + 2A^-$$

<div align="center">Precipitated</div>

2. *Lyophilic Sol.*

$$\boxed{\begin{array}{ccc} H_2O & & H_2O \\ & \boxed{\begin{array}{c} Starch \\ OH^- \end{array}} & \\ H_2O & & H_2O \\ H_2O & & H_2O \end{array}} \quad H^+$$
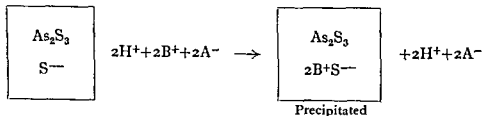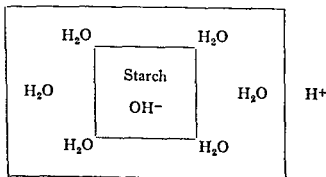
THE INTERFACE

Since the particles in a sol are small compared with those in a suspension the area of the interface between disperse phase and dispersion medium is very much greater in the colloidal solution than in the suspension. Many of the peculiar properties of sols are due to adsorption, particularly of ions, at this large interface.

LYOPHOBIC AND LYOPHILIC SOLS

Sols may be divided into two classes, which differ in the ease with which the disperse ph   itated, and are called *lyophobic* [1] (easil   t easily coagulated). The following   between these two classes. *There are many exceptions to these generalisations.*

	Lyophobic [2] Sols	Lyophilic [2] Sols
Cause of stability.	Electrical charges on particles, which repel one another.	Presence of a sheath of solvent molecules [3] round particles ; also (less important) electrical charges on particles.
Coagulation.	Coagulated by traces of electrolytes,[4] which discharge the particles.	*Not* coagulated by traces of electrolytes. Coagulated by high concentrations of electrolytes or of other substances, which remove the layer of solvent molecules from the particles.
Reversibility.	Particles, if coagulated by an electrolyte, are *not* readily redispersed.	Particles, if coagulated, are readily redispersed by adding more dispersion medium.
Concentration of disperse phase.	Always low.	May be high.
Viscosity.	Practically the same as that of the dispersion medium.	Often high.
Gel formation.	Do *not* form gels.	Many form gels.

[1] These terms mean " solvent-hating " and " solvent-loving " respectively.
[2] If the dispersion medium is water, the terms " hydrophobic " and " hydrophilic " are used.
[3] The particles behave in some ways as if they were liquids. Lyophilic sols are sometimes called " emulsoids," and lyophobic sols " suspensoids."
[4] The ion of charge opposite to that of the colloidal particles is responsible for precipitation. Multivalent ions are more efficient than univalent ions.

latter's particles. Thus proteins (Prt) when negatively charged may be precipitated by ferric hydroxide.

$$Prt^- + FH^+ \longrightarrow Prt.FH$$
$$\text{neutral, coagulated}$$
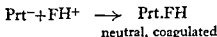
If excess ferric hydroxide is added, complex positively-charged particles are produced thus :

$$Prt^- + 2FH^+ \longrightarrow [Prt.2FH]^+$$

and all the material remains in colloidal solution.

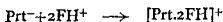Experiments illustrating these principles are described on pp. 171-172 and 405-406.

PROTECTION OF LYOPHOBIC SOLS BY LYOPHILIC SOLS

When lyophobic and lyophilic sols carrying charges of the *same* sign are mixed, the lyophilic sol confers some of its properties on the lyophobic sol, which is no longer coagulated by small quantities of electrolytes. This is called *protection*. It is thought that the disperse phase of the lyophilic sol forms a coating round the particles of the lyophobic sol. (Experiment, see p. 172.)

GELS

Gels are colloidal solutions formed by cooling concentrated lyophilic sols (*e.g.*, of gelatin or of starch in water). They have the mechanical properties of solids ; it is thought that the dispersion medium is a liquid (*e.g.*, water) containing a mass of interlocking particles of disperse phase. Gels may be transformed into sols again on heating. (Experiment, see p. 172.)

FURTHER READING

INTRODUCTORY TEXT-BOOKS

HOLMYARD, E. J. Elementary Chemistry, 3rd edition. Arnold, London, 1934.

LITTLER, W. Elementary Chemistry, revised edition. Bell, London, 1937.
 (Either of these books will lay the foundations for the physical chemistry considered here.)

FREUND, I. The Study of Chemical Composition. Cambridge University Press, 1904. (Out of print.)
 (Gives an excellent historical account of the principles of chemistry, illustrated with quotations.)

The starch particle has a sheath of loosely-combined water molecules round it. It may have adsorbed cations (*e.g.*, hydroxyl), although this is not necessary for stability.
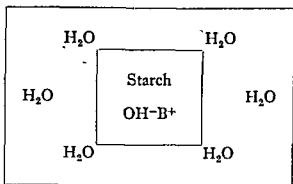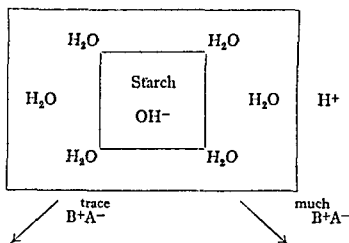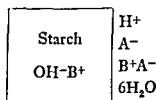
The behaviour of the sol with a trace of an electrolyte and with much electrolyte is represented above. The particle shown at I is neutral but is still hydrated, and therefore does not coalesce with its fellows. The particle shown at II has been neutralised and stripped of its layer of water molecules. It therefore coalesces with its fellows, and the sol is coagulated.

If two colloidal solutions containing particles of opposite charge are mixed in such proportions that the charges on the particles neutralise one another, both sols are coagulated. For example, ferric hydroxide (positive, FH⁺) and arsenious sulphide (negative, AS⁻) sols precipitate one another.

$$FH^+ + AS^- \longrightarrow [FH.AS]$$
$$\text{neutral, coagulated}$$
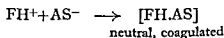
In some cases, where lyophilic sols are concerned, the addition of an excess of one sol to another results in a *reversal* of the sign on the

VOLUMETRIC ANALYSIS

GENERAL

This Chapter must be read in conjunction with Chapter 3 (General Ideas on Quantitative Work) and the relevant sections of Chapters 5 (Measurement) and 6 (Principles of Physical Chemistry).

7, 1   METHODS OF QUANTITATIVE ANALYSIS

The purely chemical methods of quantitative analysis are gravimetric and volumetric. Both depend on the fact that substances interact in constant proportions by weight. Other methods of quantitative analysis, *e.g.*, gas-volumetric, colorimetric, spectrographic, depend on the measurement of properties other than weight.

7, 2   PRINCIPLES OF GRAVIMETRIC ANALYSIS

In gravimetric analysis a substance (A) is brought into solution and then transformed into an insoluble substance (B) of known composition, which is filtered and weighed. If the equivalents of A and B are known, the weight of A taken can be calculated by simple proportion. In general, only reactions which go to completion, and which are specific for the substance concerned, are useful as the basis of gravimetric methods. Gravimetric analysis is not considered further in this book, since it is impossible in most medical courses to provide the time required.

7, 3   PRINCIPLES OF VOLUMETRIC ANALYSIS

Volumetric analysis is the only quantitative work done in most medical chemistry courses. It is therefore important, not only for its own sake, but because it illustrates many general ideas common to all quantitative scientific work, which have been discussed in Chapter 3, and because it gives practice in some methods of accurate measurement, details of which will be found in Chapter 5. Frequent reference to these chapters will be necessary before and during the volumetric experiments.

In volumetric analysis a known volume of a solution whose concentration is to be determined (called the "*unknown*" *solution*) is taken, and a second solution, containing a known concentration of another substance (called the *standard solution*), is added to the first until reaction is complete. This process is called a *titration*. The following conditions must be fulfilled :—(1) the proportions by weight in which the two substances react must be known ; (2) the reaction must go to completion ; (3) the reaction must be specific for the

FREUND, I. The Experimental Basis of Chemistry. Cambridge University Press, Cambridge, 1920.

(Gives full details of experiments illustrating the principles of chemistry.)

The two books by FREUND, if used in conjunction with more recent books, should facilitate a real understanding of the nature of chemistry and a training in scientific method.

ELEMENTARY PHYSICAL CHEMISTRY TEXT-BOOKS

FINDLAY, A. Physical Chemistry for Students of Medicine, 2nd edition. Longmans, Green, London, 1931.

WEST, E. S. Physical Chemistry for Students of Biochemistry and Medicine. Macmillan, New York, 1944.

KERRIDGE, P. M. T. Principles of Physical Chemistry for Medical Students. Oxford University Press, London, 1927.

PHILBRICK, F. A. An Introduction to Physical Chemistry. Dent, London, 1937.

MORE ADVANCED TEXT-BOOKS

TAYLOR, H. S., and TAYLOR, H. A. Elementary Physical Chemistry, 3rd edition. Van Nostrand, New York, 1942.

MEE, A. J. Physical Chemistry. Heinemann, London, 1934.

GLASSTONE, S. Text-Book of Physical Chemistry. Macmillan, London, 1940.

BULL, H. B. Physical Biochemistry. Wiley, New York, 1943.

SIDGWICK, N. V. The Electronic Theory of Valency. Oxford University Press, London, 1927.

(Considers valency and molecular constitution in terms of the Rutherford-Bohr atom.)

WELLS, A. F. Structural Inorganic Chemistry. Clarendon Press, Oxford, 1945.

(Deals particularly with knowledge gained from recent work on the solid state.)

THEORY OF ANALYTICAL PROCESSES

VOGEL, A. I. A Text-Book of Qualitative Chemical Analysis, 3rd edition. Longmans, Green, London, 1945.

VOGEL, A. I. A Text-Book of Quantitative Inorganic Analysis. Longmans, Green, London, 1944.

SMITH, T. B. Analytical Processes—A Physico-Chemical Interpretation, 2nd edition. Arnold, London, 1940.

The gram-equivalent of an acid is the weight of the acid which contains 1·008 g. of hydrogen replaceable by a metal.

The gram-equivalent of a base is the weight of the base which neutralises 1 gram-equivalent of any acid.

If two soluti··· ···ontaining 1 gram-equivalent of an gram-equivalent of a base per litre, ···ual volumes of these two solutions neutralise one another. Similarly, if the two solutions each contain 2 gram-equivalents per litre, equal volumes again neutralise each other. Furthermore, ·· solution containing 1 gram-equivalent of ·· solution containing 0·1 gram-equivalent ·· then 10 volumes of the base solution exactly neutralise 1 volume of the acid solution.

From the definition of gram-equivalent it follows that in *any* titration *when the reaction is complete*,

The number of gram-equiva-   The number of gram-equiva-
lents of the one substance =   lents of the other substance
titrated   run in from the burette.

If this fundamental equation, together with the terms "gram-equivalent" and "normality" (see the following section), is thor-oughly understood, no calculation in volumetric analysis will be difficult. Before the fundamental equation is applied to an example, the term "normality" will be considered.

7, 5   NORMALITY

The term "normality of a solution" is simply an expression or "the number of gram-equivalents of dissolved substance in 1 litre of the solution." *E.g.*, a solution containing 0·107 gram-equivalent of hydrochloric acid per litre is said to have a normality of 0·107, or to be 0·107 normal (written 0·107N).

The relation between ······· ·· ········ ·· ·· ·····ormality and gram-equiv··· ·· ·· ·· ·

CONCENTRATION (in grams per litre)=NORMALITY×GRAM-EQUIVALENT.

In the example mentioned in the previous paragraph,

Normality   =   0·107
Gram-equivalent of hydro-
  chloric acid   =   36·47 g.
Concentration   =   0·107×36·47=3·90 g. HCl per litre.

7, 6   CALCULATIONS

The calculation of a titration result using normalities is made as follows. Suppose the standard solution is put in the burette. The number of gram-equivalents run from the burette into the titration flask can be calculated from the normality and the volume of solution run in, both of which are known. From the fundamental equation,

substance being determined in the experimental conditions, and (4) there must be some means of knowing when the reaction is complete.

The sample of the " unknown " solution is usually measured by means of a *pipette* into a flask, beaker, or basin, and the standard solution is added gradually from a *burette* until the reaction is complete. In most cases it is necessary to add a third substance, known as an *indicator*, which undergoes a visible change at the *end-point* (the point where the reaction is complete).

For the benefit of beginners this section and the succeeding sections 7, 4 to 7, 8 refer to acid-base titrations. The principles involved apply generally to other types of titration—precipitation methods and oxidation-reduction methods. The indicators used in acid-base titrations are substances which are differently coloured in acidic and alkaline solutions, and which therefore change colour when a sample of acid or alkali has just been neutralised (for explanation when required, see pp. 100-108).

These principles may be illustrated by an example showing the calculations which follow the practical work.

*Determination of the Concentration of Sodium Hydroxide in a Solution
" A " by means of a Standard Solution " B " containing 100 g.
Hydrochloric Acid per Litre.*

It is known from the experience of previous workers that 1·00 g. of HCl reacts with 1·10 g. of NaOH.

Suppose that 10·00 ml. of solution " A " were taken ; litmus was added as indicator ; solution " B " was added until the mixture changed colour from blue to purple (end-point). Suppose the volume of solution " B " required was 7·40 ml. (This volume is known as the " titre.") Therefore the weight of HCl added was

$$\frac{7 \cdot 40 \times 100}{1000} = 0 \cdot 740 \text{ g.}$$

0·740 g. HCl react with 0·740×1·10 g.=0·814 g. NaOH. Therefore 10·00 ml. of solution " A " contain 0·814 g. sodium hydroxide, and 1 litre of solution " A " contains

$$\frac{0 \cdot 814 \times 1000}{10} = 81 \cdot 4 \text{ g. sodium hydroxide.}$$

It is sometimes convenient to take a known volume of the standard solution in the flask and to add the " unknown " solution from the burette. Although the calculation is different, the principles are the same as in the above example.

7, 4   GRAM-EQUIVALENTS

Calculations in volumetric analysis are simplified if the concentrations of solutions are expressed in gram-equivalents per litre instead of grams per litre.

Thence, by definition of normality,[6] normality of sodium hydroxide solution " C "=0·0910.

Gram-equivalent of sodium hydroxide is 40·0 g., therefore concentration of sodium hydroxide in solution " C "=0·0910×40·0= 3·64 g. per litre.

Result.[7] Solution " C " contains 3·64 g. sodium hydroxide per litre.[8]

Points to Note.

1. Date every piece of work.

2. State clearly and briefly in the heading what you are trying to do.

3. Describe the work so that another person (who understands what a titration is) could repeat it without discussing it personally with you. State solutions used, giving the letters or numbers of the samples, indicator used and end-point.

4. Report the *actual burette readings* (not the differences between them) while you are doing the work.

5. At least two results concordant within the limits of random variation (0·10 ml.) must be obtained. No one can safely trust to a single determination.

6. The following common-sense rule provides a rough check on the accuracy of the arithmetic :—

If the volume of the unknown solution used is greater than the volume of the standard solution, the unknown normality must be less than the normality of the standard solution, and vice versa. .

7. State the final result boldly and clearly. Always state *units*.

8. Express the result so as to show its precision. Give the same number of significant figures as in the least precise observation.

7, 8   CONDUCT OF A TITRATION

This section describes the general method of carrying out a titration. Instructions for the handling of pipettes and burettes are given on pp. 59-60 and 63.

1. Make sure that the solutions are homogeneous.

2. See that all apparatus is clean, and that the burette-tap is well-greased but *not* clogged.

3. Wash out the burette and pipette each three times with *small* volumes of the solutions to be measured in them. (This ensures that the solutions are not diluted by water previously used for washing.)

4. Wash out the conical flask with distilled water.

5. Fill the burette with the solution to be used, clamp it vertically, and adjust the meniscus exactly to a graduation mark (usually the zero mark for the first titration). If a funnel is used to fill the burette, remove it before adjusting the meniscus.

6. Pipette a portion of the other solution into the conical flask and add indicator if required (2 drops, unless otherwise stated).

the number of gram-equivalents of the substance being determined, which were put into the titration-flask at the start, is *equal* to this. The volume of the " unknown " solution put into the flask at the start being known, the concentration of this solution in gram-equivalents per litre (normality) or in grams per litre can be calculated. An example is given below.

7, 7   REPORTS

This section will serve as a model for students' reports of their own work. Special attention should be paid to the points mentioned in footnotes.

This section also illustrates the use of the term " normality " more clearly than can be done in words in the preceding section.

17 Apr. 1945.[1]

Determination of Sodium Hydroxide in Solution " C," by means of Standard Hydrochloric Acid Solution " D " [2]

Equation for reaction,
$$NaOH + HCl = NaCl + H_2O.$$

10·00 ml. NaOH solution " C " pipetted into flask in each titration. Indicator used : Bromophenol blue.

Standard 0·103N-HCl solution " D " run in from burette as follows (end-point, colour change violet to brown) [3]:

Titration		I.	II.	III.
Burette Reading at start	.	0·00	8·95	17·75 ml.[4]
„ „ at end-point	.	8·95	17·75	26·55 „
Volume of " D " used	.	8·95	8·80	8·80 ml.

Titration I. is discordant—therefore ignored.
Taking the average of the other two results,[5]

10·00 ml. solution " C " = 8·80 ml. 0·103N-HCl solution " D."

8·80 ml. 0·103N-HCl solution contains

$$\frac{8·80 \times 0·103}{1000} = \frac{0·910}{1000} \text{ gram-equivalents HCl.}$$

These must have reacted with an *equal* number of gram-equivalents of NaOH, therefore 10·00 ml. solution " C " must contain

$$\frac{0·910}{1000} \text{ gram-equivalents NaOH.}$$

Therefore 1 litre of solution " C " contains

$$\frac{1000 \times 0·910}{10·00 \times 1000} = . \; 0·0910 \text{ gram-equivalents NaOH.}$$

SIMPLIFIED METHODS OF CALCULATION

The method of calculation set out on pp. 132-133 is lengthy, but has the advantage that it impresses on the student the fundamental principles of volumetric analysis every time he does a calculation.

When the student is familiar with the principles, he may use any shorter method of calculation (*e.g.*, the method given below) so long as he understands what he is doing.

When more complicated calculations have to be done (*e.g.*, in a " back titration "—see pp. 136-137) it always pays to go back to first principles and think in terms of the number of gram-equivalents of substances used in the titration.

Example.

Using the data given on p. 132,

Suppose the normality of solution " C " is x, then

$$\text{10 00 ml. } x\text{N-NaOH solution} \quad = \quad 8\cdot80 \text{ ml. } 0\cdot103\text{N-HCl solution,}$$

therefore

$$10\cdot00 \times x = 8\cdot80 \times 0\cdot103,$$

therefore

$$x = \frac{8\cdot80 \times 0\cdot103}{10\cdot00} = 0\cdot0910,$$

i.e., the normality of the sodium hydroxide " C " is 0·0910.

(The concentration of " C " in grams per litre is then calculated as shown on p. 133.)

OTHER METHODS OF DESCRIBING CONCENTRATIONS

1. Concentrations in gram-molecules per litre.

Where a substance has two or more different equivalents in different reactions (*e.g.*, phosphoric acid), normalities are ambiguous. Confusion is avoided by describing the concentrations of solutions in gram-molecules per litre. A solution containing 0·123 g. mols. per litre is called " 0·123 *molar* " (written " 0·123M ").

2. Special concentrations for applied work.

While the chemist likes to think in terms of gram-equivalents or gram-molecules, the person who uses analytical results for other purposes often prefers to think in other units, *e.g.*, parts per 100,000 in water analysis, milligrams per 100 ml. (mg. per cent.) in the determination of blood constituents. It is often convenient, when applying volumetric methods in fields other than pure chemistry, to make up standard solutions of such concentration that the titres give the quantity to be determined without further calculation.

SOLUTIONS OF WIDELY DIFFERING NORMALITIES

Two solutions of widely differing normalities cannot be accurately titrated against one another. The precision of a titration depends

7. Read the burette. Note the result in your book, and check by re-observation before doing anything else.

8. Place the conical flask on a piece of white paper or a white tile under the burette. Shake the flask gently with your right hand, and run in the solution from the burette, turning the tap with your left hand. (This method seems clumsy at first but has two advantages, viz.: (1) you are pressing the tap into its socket; (2) the body of the tap provides some support for your hand, which is valuable during the careful addition of the last few drops of solution.)

9. When the changes in colour in the flask suggest that the end-point is near, wash down the inside of the flask with the fine jet of your wash-bottle and continue adding the solution from the burette drop-wise, while shaking the flask. If you suspect that any of the solution from the burette is adhering to the upper part of the flask, wash down again.

10. When the end-point is reached, read the burette again to the nearest half-graduation (i.e., if the burette is graduated in 0·10 ml., read it to 0·05 ml.). Note the result and check it as before.

11. Repetition of determination. Precision.

The titration must now be repeated. If the two titres agree within 0·10 ml. (1% variation on 10 ml. titre), they may be considered as concordant and the arithmetical mean of the titres used for the calculation. If the titres do *not* agree within 0·10 ml. further titrations must be done until concordant results (as defined above) are obtained.

12. Accuracy.

The author's practice is to consider a student's results satisfactory if the arithmetical mean of the titres is within 0·10 ml. of the correct titre.

7, 9   MISCELLANEOUS POINTS

Beginners should read this section only after they have done several titrations and have become familiar with the principles and simple practice of volumetric analysis.

THE TRUE PURPOSE OF A TITRATION

The true purpose of a titration is to determine, *not e.g.*, " the concentration of solution X," but " the concentration of constituent Y in solution X." In order to simplify matters the previous sections of this chapter have referred to solutions containing only one dissolved substance, where the above two expressions mean the same thing. The student must now realise that a titration tells him merely the concentration of a particular constituent in his " unknown " solution and he must always be clear what this constituent is.· In most of the titrations described here, the constituent determined is an *ion*—e.g., in the titration of an acid with standard alkali, actual or potential hydrogen ion.

with excess of a strong base (*e.g.*, sodium hydroxide) the ammonia is expelled from solution quantitatively.

$$NH_4^+ + OH^- = NH_4OH \rightleftharpoons NH_3\uparrow + H_2O.$$
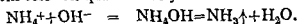
The excess of strong base can then be determined by titration with standard acid.

The calculation may be done as in the following example :

10·00 ml. xN-NH$_4$Cl solution " Y " and 10·00 ml. NaOH solution " B " (0·2050N) were boiled together until all NH$_3$ had been evolved. Excess NaOH required 8·50 ml. HCl solution " C " (0·1045N). (Average of two concordant results.)

Volumes of standard alkali present at the start and of standard acid used in the back titration are converted into the equivalent volumes of *normal* solutions.

10·00 ml. 0·2050N-NaOH $\equiv$ 2·050 ml. 1N-NaOH (NaOH at start)
8·50 ml. 0·1045N-HCl $\equiv$ 8·50×0·1045 ml.
$\equiv$ 0·888 ml. 1N-NaOH (NaOH in excess),

subtracting

10·00 ml. xN-NH$_4$Cl$\equiv$1·162 ml. 1N-NaOH (NaOH used by NH$_4$Cl).

Therefore x (the normality of NH$_4$Cl solution " Y ")

$$= \frac{1·162 \times 1·000}{10·00} = 0·1162.$$

7, 11   SOURCES OF ERROR IN TITRATION

This section, based on the very thorough treatment by Conway, *Micro-Diffusion Analysis and Volumetric Error*, Crosby Lockwood, 1939, is included for reference only.

The sources of error and variation in titration may be classified as follows. Brief notes on the relative importance of the sources *in 10-25 ml. scale titrations*, and of the ways in which greater accuracy or precision may be obtained, are added.

Group	Sources of Errors and Variations	Relative Importance	Methods of Eliminating or Reducing Error
I. Constant Errors (Glass).	Temperature different from that at which glass-ware was standardised.	Negligible over range 15°-25°.	Corrections may be applied in very accurate work.
	Pipette inaccurate. Burette inaccurate. Graduated flask inaccurate.	All may be large or small.	Re-calibrate or use standard apparatus.

not on the absolute value of the random variation in ml. but the ratio of that variation to the total titre. In titrations here the random variation is ± 0.05 ml. Thus if in a certain determination the titre is 10.20 ml. (*i.e.*, 10.20$\pm$0.05 ml.), the random variation is $\pm \dfrac{0.05}{10.20}$ or $\pm 0.5\%$, which for the present work is a reasonable standard of accuracy. If, however, the titre in another determination is 1.20 ml. (*i.e.*, 1.20$\pm$0.05 ml.), the random variation is $\pm \dfrac{0.05}{1.20}$ or about $\pm 5\%$; no result depending on the determination can possibly have greater precision than this.

To standardise a solution, the normality of which is known to be more than about three times as great as that of the standard solution, the following method should be used. (1) Dilute the more concentrated solution *in a known ratio to obtain a solution whose normality is roughly equal to that of the standard solution.* (For example, if an approximately 1N hydrochloric acid solution is to be standardised by means of 0.1N sodium carbonate solution, dilute the hydrochloric

⋮

solution by titration against the standard. (3) Calculate the normality of the original concentrated solution.

7, 10   BACK TITRATIONS

Many determinations which cannot be done by direct titration can be done indirectly by back titration.

Suppose a substance A reacts with B to give a product X (which can be removed from the reaction-mixture, or which does not interfere with subsequent operations), and suppose that B can be titrated with C.

$$A + B = X$$
$$B + C = Z.$$

Suppose a solution of A is treated with a quantity of B known to be in *excess* of that required to react with all the A present; the product X is removed, if necessary, and the excess of B is determined by titration with C. For example,

$$A + 2B = X + B$$
$$B + C = Z.$$

The amount of B present at the start is known, and the amount of B which did *not* react with A is known from the titration; therefore, by subtraction, the amount of B which *did* react with A is known. Hence the amount of A present in the original solution can be calculated.

An example of a determination carried out by back titration is the determination of ammonium salts. If an ammonium salt is boiled

STANDARD SOLUTIONS

All volumetric analysis depends ultimately on the *weighing of pure substances*. Weighed quantities of pure substances can be used to standardise solutions in either of the two following ways.

1. Several samples of pure substance are weighed and dissolved separately in water, and the whole of each sample is titrated with the solution to be standardised.

2. One sample of pure substance is weighed out, and dissolved in water ; the solution is made up to a known volume in a graduated flask giving a standard solution ; known volumes of this solution are then titrated with the solution to be standardised.

Method 1 is preferable in advanced work, since an error in weighing is easily detected, while in method 2 an error in weighing or in the preparation of the standard solution will go unnoticed, since there is no duplicate determination to check this part of the work.

In elementary work, however, method 2 is customary, since few laboratories have sufficient balances to permit the multiple weighings which method 1 demands. The following instructions are based on the use of method 2.

7, 12   CHOICE OF STANDARDS

Substances chosen for the preparation of standard solutions (called *primary standards*) must be available in a pure condition. They must be stable in the solid state (preferably at 110-120°, so that they may be dried at this temperature), and in solution. They must not be hygroscopic. The reactions between the standard solution and those solutions to be standardised against it must go to completion. The standards should preferably have high equivalent weights so that percentage errors in weighing are as small as possible. Substances for use as primary standards are listed in the appropriate sections below.

7, 13   PREPARATION OF A STANDARD SOLUTION

Example—PREPARATION OF STANDARD SODIUM CARBONATE SOLUTION

Sodium carbonate (Na_2CO_3) of analytical reagent (A.R.) quality, which has been dried by heating to 260°-270° for half an hour, is provided in a weighing bottle.

Weigh the bottle and contents to the nearest 0·0005 g. Tip out into a clean dry 200 ml. beaker about 2·65 g. sodium carbonate and

The difference
carbonate in the
ker by pouring
on to it *boiling* water (about 20 ml.), and cool the solution by adding cold water until the beaker is about two-thirds full. Transfer the solution quantitatively to the 500 ml. graduated flask (see p. 28) and make up to the mark with water. Stopper the flask with its own ground-glass stopper or a sound clean cork, and mix the solution

Group	Sources of Errors and Variations	Relative Importance	Methods of Eliminating or Reducing Error
II. Constant Errors (Chemical).	Impurity of substance used as standard.		Use pure substance.
	Error in concentration of standard solution.		Make fresh solution.
	End-point not the same as the point of chemical-equivalence.	All may be large or small.	Standardise the method (i) by doing titrations with known weights of pure substances and drawing a graph to relate titres and weights of substance determined; or (ii) by doing titrations with indicator and water only and subtracting the "indicator-blank" so determined from all other titres.
	This may be due to one of two reasons, (i) the titration-reaction is not quantitative, (ii) an appreciable volume of the burette-solution is necessary to produce a visible change in colour when the indicator alone is titrated.		
			Error may be reduced by using more concentrated solutions.
III. Random Variation (Glass).	Size of drop used to produce colour change at end-point.	Large.	Reduce size of drop or remove part of drop from jet with glass rod, or immerse tip of burette in reaction mixture.
	Error in reading burette at end-point.	Moderate.	Use burette-reader and lens to estimate tenths of a graduation.
	Error in reading burette at zero-mark at start of titration.	Negligible.	Use burette-reader and lens. (It is easier to set the meniscus on a definite mark, than to estimate tenths of a graduation accurately.)
	Variation in pipette or burette delivery.	Negligible (if care is used).	Precise attention to instructions for use of apparatus necessary.
IV. Random Variation (Chemical).	Difficulty in deciding exact shade of colour to be taken as end-point.	May be large.	Decide on a colour standard, and titrate to this colour in all cases. Use more concentrated solutions if possible.

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Weigh the bottle and contents to the nearest 0·0005 g. Tip out into a clean dry 200 ml. beaker about 2·65 g. sodium carbonate and remove the bottle and contents to the . . . . . The difference . . . . carbonate in the . . . . ker by pouring on to it *boiling* water (about 20 ml.), and cool the solution by adding cold water until the beaker is about two-thirds full. Transfer the solution quantitatively to the 500 ml. graduated flask (see p. 28) and make up to the mark with water. Stopper the flask with its own ground-glass stopper or a sound clean cork, and mix the solution

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	Error in reading burette at zero-mark at start of titration.	Negligible.	Use burette-reader and lens. (It is easier to set the meniscus on a definite mark, than to estimate tenths of a graduation accurately.)
	Variation in pipette or burette delivery.	Negligible (if care is used).	Precise attention to instructions for use of apparatus necessary.
IV. Random Variation (Chemical).	Difficulty in deciding exact shade of colour to be taken as end-point.	May be large.	Decide on a colour standard, and titrate to this colour in all cases. Use more concentrated solutions if possible.

four significant figures. The weighing is carried to five significant figures here only to give the student practice.

4. Anhydrous sodium carbonate does not dissolve readily in cold water. A little boiling water dissolves it almost immediately.

5. Hot solutions must *not* be introduced into graduated apparatus.

6. If the solution when prepared is *not* homogeneous the titres will vary widely, thus, *e.g.*, 8·85, 9·40, 10·20, 10·35 ml.; in this case the time spent in accurate weighing and in transferring the sample to the graduated flask has been wasted.
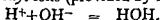
7. Solutions should be kept in a cool, dark place. If a half-filled flask is allowed to stand, drops of water may condense on the upper part of the flask. The solution must always be shaken immediately before use to ensure that it is homogeneous.
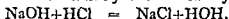
ACID-BASE TITRATIONS

7, 14   ## INTRODUCTION

The simplest examples of volumetric analyses are acid-base titrations, in which a standard solution of an acid is used to determine the concentration of a solution of a base, or vice versa. The essential reaction in all cases is the combination of *hydrogen* ions (provided by the acid) and *hydroxyl* ions (provided by the base) to form water.
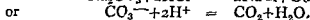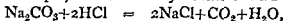
$$H^+ + OH^- = HOH.$$

Example—titration of sodium hydroxide with hydrochloric acid:
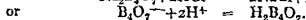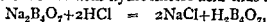
$$NaOH + HCl = NaCl + HOH.$$

In general, any soluble base and any soluble acid may be used in these determinations, but weak acids and weak bases cannot be titrated against each other. Hydrochloric, sulphuric, and nitric acids are strong acids; acetic, oxalic, benzoic, and most other organic acids are weak. Sodium, potassium, calcium, and barium hydroxides are strong bases; ammonium hydroxide is weak.

In addition to bases proper . . . . strong acids if the appropriate indicator (see p. 142) is used. Sodium carbonate, for example, reacts with hydrochloric acid as follows:

$$Na_2CO_3 + 2HCl = 2NaCl + CO_2 + H_2O,$$

or

$$CO_3^{--} + 2H^+ = CO_2 + H_2O.$$

Sodium borate reacts with hydrochloric acid thus:

$$Na_2B_4O_7 + 2HCl = 2NaCl + H_2B_4O_7,$$

or

$$B_4O_7^{--} + 2H^+ = H_2B_4O_7.$$

EQUIVALENTS

The *gram-equivalent* of an *acid* is the weight of the acid which contains 1·008 g. of hydrogen replaceable by a metal.

The *gram-equivalent* of a *base* is the weight of the base which neutralises 1 gram-equivalent of any acid.

thoroughly by inverting the flask and shaking hard a dozen times.
Label the flask as follows (for calculation of normality see below):

> Sodium Carbonate
> Solution " A " 0·1023N
> A. Brown.
>   2 May 1945

Report.
The following form of report is suggested:

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2 May 1945.
Preparation of Standard Sodium Carbonate Solution " A."

1st weight of bottle+sodium carbonate .	.	32·8725 g.
2nd „ „ „ „ .	.	30·1610 g.
Weight of sodium carbonate sample taken .	.	2·7115 g.

This sample was dissolved in water, and the volume of the solution
made up to 500 ml. in a graduated flask, giving standard solution " A."
The gram-equivalent of Na_2CO_3 is 53·00 g.

Solution "A" therefore contains $\frac{2·7115}{53·00}$ g. equiv. Na_2CO_3 in
500 ml.

„   „   „   „ $\frac{2·7115}{53·00} \times 2 = 0·1023$ g. equiv.
Na_2CO_3 per litre.

Sodium Carbonate Solution " A " is 0·1023N.

Points to Note.
  1. In making the standard solution the analyst has a choice of two
slightly different methods.
  (*a*) He may weigh accurately a sample which, when dissolved, gives
500 ml. *exactly* 0·1000N solution (here 2·650 g. sodium carbonate).
  (*b*) He may weigh accurately a sample which, when dissolved,
gives 500 ml. of a solution which is *approximately* decinormal.
  In method (*a*) the weighing takes a little longer because the sample
weight has to be adjusted exactly, but no calculation is necessary to
find the normality of the standard, and it is easy to calculate normalities
of solutions titrated with this. In method (*b*) the weighing is quicker,
but time has to be spent in calculating the normality of the standard
solution, and subsequent calculations are more tedious.
  2. Weights must be noted in your book, *not* on rough-paper, while
the weights are on the pan.
  3. Since burette readings will be four significant figures at the
most, the weight of the sample need not be determined to more than

four significant figures. The weighing is carried to five significant figures here only to give the student practice.

4. Anhydrous sodium carbonate does not dissolve readily in cold water. A little boiling water dissolves it almost immediately.

5. Hot solutions must *not* be introduced into graduated apparatus.

6. If the solution when prepared is *not* homogeneous the titres will vary widely, thus, *e.g.*, 8·85, 9·40, 10·20, 10·35 ml.; in this case the time spent in accurate weighing and in transferring the sample to the graduated flask has been wasted.

7. Solutions should be kept in a cool, dark place. If a half-filled flask is allowed to stand, drops of water may condense on the upper part of the flask. The solution must always be shaken immediately before use to ensure that it is homogeneous.

ACID-BASE TITRATIONS

7, 14

INTRODUCTION

The simplest examples of volumetric analyses are acid-base titrations, in which a standard solution of an acid is used to determine the concentration of a solution of a base, or vice versa. The essential reaction in all cases is the combination of *hydrogen* ions (provided by the acid) and *hydroxyl* ions (provided by the base) to form water.
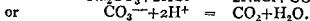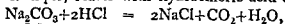
$$H^+ + OH^- = HOH.$$

Example—titration of sodium hydroxide with hydrochloric acid:
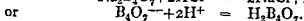
$$NaOH + HCl = NaCl + HOH.$$

In general, any soluble base and any soluble acid may be used in these determinations, but weak acids and weak bases cannot be titrated against each other. Hydrochloric, sulphuric, and nitric acids are strong acids ; acetic, oxalic, benzoic, and most other organic acids are weak. Sodium, potassium, calcium, and barium hydroxides are strong bases ; ammonium hydroxide is weak.

In addition to bases proper—*i.e.*, hydroxides—certain soluble salts of strong bases and weak acids behave like weak bases due to hydrolysis (see pp. 95-96) and their solutions can be titrated as bases with strong acids if the appropriate indicator (see p. 142) is used. Sodium carbonate, for example, reacts with hydrochloric acid as follows :

$$Na_2CO_3 + 2HCl = 2NaCl + CO_2 + H_2O,$$

or

$$CO_3^{--} + 2H^+ = CO_2 + H_2O.$$

Sodium borate reacts with hydrochloric acid thus :

$$Na_2B_4O_7 + 2HCl = 2NaCl + H_2B_4O_7,$$

or

$$B_4O_7^{--} + 2H^+ = H_2B_4O_7.$$

EQUIVALENTS

The *gram-equivalent* of an *acid* is the weight of the acid which contains 1·008 g. of hydrogen replaceable by a metal.

The *gram-equivalent* of a *base* is the weight of the base which neutralises 1 gram-equivalent of any acid.

The *gram-equivalent* of a weak-acid strong-base *salt* (such as sodium carbonate) is the weight of the salt which reacts with 1 gram-equivalent of a strong acid.

INDICATORS

In acid-base titrations the reaction is *not* accompanied by a colour change. (Contrast permanganate titrations, p. 153.) It is necessary, therefore, to add an indicator, *i.e.*, a substance which has different colours in acid and in alkaline solution.

The choice of indicators in acid-base titrations is considered at length with reference to titration curves on pp. 100-108. The following instructions are intended for the use of students who have not yet studied hydrogen-ion concentration.

Type of acid	Type of base	Suitable Indicators	Colour of Indicator	
			In acid solution	In alkaline solution
Strong	Strong	Bromothymol blue [1]	Yellow	Blue
		Bromophenol blue [1,2]	Yellow	Violet
Strong	Weak	Methyl red	Red	Yellow
		Bromophenol blue [1]	Yellow	Violet
Weak	Strong	Phenolphthalein	Colourless	Pink
Strong	Carbonate Borate	Bromophenol blue [1]	Yellow	Violet

STANDARD SOLUTIONS

The following substances can be weighed out accurately for the preparation of standard solutions.

Substance	Type	Equivalent
Sodium carbonate Na_2CO_3 . . . Sodium borate (borax) $Na_2B_4O_7$, $10H_2O$.	Weak-acid strong-base salt.	Half molecular weight.
Potassium bi-iodate $H.K(IO_3)_2$ . .	Strong acid.	Equal to molecular weight.
Potassium hydrogen phthalate $H.KC_8H_4O_4$	Weak acid.	Equal to molecular weight.
Succinic acid $H_2.C_4H_4O_4$ . . .	Weak acid.	Half molecular weight.

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base solution is *not* contaminated with carbonate

Standard solutions of other acids and bases, *e.g.*, hydrochloric acid,[1] sulphuric acid, and sodium hydroxide cannot be prepared by direct weighing ; solutions of these of approximately known normality must be made up as under and then standardised by titration.

Substance	Quantity required for 500 ml. approximately 0·1N Solution
Hydrochloric acid .	4·5 ml. concentrated acid
Sulphuric acid . .	1·5 ml. ,,
Nitric acid . .	3·0 ml. ,,
Acetic acid . .	3·0 ml. " glacial " acid
Ammonium hydroxide .	3·5 ml. concentrated (d=0·880)
Sodium hydroxide .	3·5 g.[2]
Potassium hydroxide .	5·0 g.[2]

7, 15 STANDARDISATION OF STRONG ACID AGAINST CARBONATE

Equation for reaction. $2H^+ + CO_3^{--} = H_2CO_3$.

Standard solution. Sodium carbonate (approximately 0·1N) (prepared as described on pp. 139-141).[3]

Unknown solution. Hydrochloric, sulphuric or nitric acid (approximately 0·1N).

Solution in burette. Acid.

Indicator. Bromophenol blue (2 drops).

End-point. Violet—*dull brown*[4]—yellow.

Titration Curve. See p. 101.

7, 16 STANDARDISATION OF STRONG BASE AGAINST STRONG ACID

Equation for reaction. $H^+ + OH^- = HOH$.

Standard solution. Hydrochloric, sulphuric or nitric acid (approximately 0·1N, standardised as described in preceding section), or potassium bi-iodate (prepared as described on pp. 139-141).

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[3] Borax may be used instead of sodium carbonate. Details are as above, except that methyl red is used as indicator. End-point, yellow-*orange*-red.

[4] The colour to be taken as end-point is shown in italics in each case.

· *Unknown solution.* Sodium or potassium hydroxide (approximately 0·1N).
   Solution in burette. Acid.
   Indicator. Bromothymol blue (2 drops).
   End-point. Blue—*green*—yellow.
   Alternative indicator. Bromophenol blue (2 drops) (to be used if alkali is contaminated with carbonate).
   End-point. Violet—*dull brown*—yellow.
· *Titration Curve.* See pp. 101 and 105.

7, 17   STANDARDISATION OF WEAK BASE AGAINST STRONG ACID

   Method as detailed in the preceding section except for the following :
   Equation for reaction. $H^+ + NH_4OH = NH_4^+ + HOH$.
   Unknown solution. Ammonium hydroxide (approximately 0·1N).
   Indicator. Methyl red (2 drops).
   End-point. Yellow—*orange*—red.
   Titration Curve. See pp. 103 and 105.

7, 18   STANDARDISATION OF STRONG BASE AGAINST WEAK ACID

   Equation for reaction. $HA + OH^- = A^- + HOH$.
   Standard solution. Potassium hydrogen phthalate ($H.KC_8H_4O_4$, monobasic) or succinic acid ($H_2.C_4H_4O_2$, dibasic) (approximately 0·1N prepared as described on pp. 139-141).
   Unknown solution. Sodium or potassium hydroxide (approximately 0·1N).
   Solution in burette. Base.
   Indicator. Phenolphthalein (2 drops).
   End-point. Colourless—*pink*.
   Titration Curve. See pp. 103 and 105.

Points to Note.

   1. The pink colour at the end-point should persist for 30 seconds. After this it fades, since the solution absorbs carbon dioxide from the air.

   2. Whenever alkali is used in the burette wash the latter thoroughly with water immediately after use, otherwise the tap will probably jam.

7, 19   DETERMINATION OF EQUIVALENT OF AN ACID

   Principle. A sample of the acid is weighed accurately, dissolved in water and the solution made up to a known volume in a graduated flask. The concentration of this solution in g. per litre is known accurately. The normality of the solution is determined by titration with

standard solution of a strong base, and the gram-equivalent of the acid calculated from the equation

Concentration (in g. per litre)=Normality×Gram-Equivalent.

Standard solution. Sodium or potassium hydroxide (approximately 0·1N, standardised as described in the previous section).

Unknown solution. Solution of acid (prepared as described on pp. 139-141 ; should be very approximately 0·1N).

Other details. If acid is strong, as in section 7, 16, pp. 143-144. If acid is weak, as in section 7, 18, p. 144.

7, 20   DETERMINATION OF AMMONIUM SALT BY BACK TITRATION

Principle and Equations. The general principles of back titrations and the methods of calculation used are discussed on pp. 136-137. If an ammonium salt is boiled with excess of a strong base (*e.g.*, sodium hydroxide), the salt is decomposed and the ammonia is expelled from solution quantitatively.

$$NH_4^+ + OH^- \ = \ NH_4OH \ = \ NH_3\uparrow + H_2O.$$
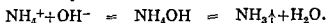
The excess of strong base is then determined by titration with standard acid.

$$OH^- + H^+ \ = \ HOH.$$

Standard solutions. Sodium hydroxide (approximately 0·2N). Hydrochloric acid (approximately 0·1N).

Unknown solution. Ammonium chloride or sulphate (approximately 0·1N).

Method. Into each of two conical flasks pipette the given ammonium chloride solution (10·00 ml.) and the standard sodium hydroxide solution (10·00 ml.). Add to each flask water (about 20 ml.), to allow for loss by evaporation, and a few porous chips to ensure smooth boiling. Boil the mixtures gently over wire gauze until the escaping steam no longer turns moist litmus-paper blue, *i.e.*, until all the ammonia has been evolved. Cool the flasks, add to the contents of each bromophenol blue (2 drops), and titrate with standard hydrochloric acid solution. If the results are not concordant within 0·10 ml. do two more determinations.

Points to Note.

1. The point during the boiling when the escaping vapours no longer turn litmus blue is just as much an end-point as the colour change in the titration ; the report must state that boiling was continued to this point.

2. If evaporation reduces the volume of the mixture greatly, add more water.

3. The boiling requires 15-20 minutes.

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7, 21   DIRECT DETERMINATION OF AMMONIUM SALT AND KJELDAHL DETERMINATION OF NITROGEN

Ammonium salts may be determined by treatment with excess caustic alkali, distillation of the liberated ammonia quantitatively from this mixture into a known quantity of standard acid, and back titration of the excess acid.

This method is much used for the determination of ammonium salts—whether pre-existing as such or formed from other nitrogenous compounds (*e.g.*, from urea by enzyme action, or from many classes of nitrogenous organic compounds by Kjeldahl's method). Kjeldahl's method consists of digesting the nitrogenous material with concentrated sulphuric acid (and additional reagents specified later). Nitrogen present in ammonium salt, amine and amide radicals is converted quantitatively into ammonium sulphate, which is then determined as outlined above. *Nitrogen present in. nitro, azo or cyanide radicals can be determined by this method only after preliminary treatment (for details see other books).* The method, which is widely used in biochemistry, is most conveniently practised in the laboratory on the micro-scale, using quantities of the order of 1-10 mg. nitrogen as described below. Blank determinations must always be carried out to determine the nitrogen (if any) present in the reagents.

The digestion-mixture contains, in addition to sulphuric acid, a catalyst to promote oxidation of the carbon and hydrogen of organic materials (*e.g.*, copper sulphate, mercury or selenium) and some substance to raise the boiling-point of the sulphuric acid (*e.g.*, potassium sulphate or phosphoric acid).

Digestion.

A solution of the nitrogenous compound (1.00 ml. ; *known to contain 5-10 mg. nitrogen)* is pipetted into a boiling-tube. *Concentrated sulphuric acid* (2.0 ml.), *potassium sulphate* (1.0 g.), copper sulphate (1 spatula-point) and a glass bead (to promote smooth boiling) are added, and the mixture is heated over a small flame (*fume cupboard*) until all the water has been driven off and, if charring has occurred, until the liquid in the tube has become pale green or blue again.

Two determinations on the substance under investigation and two blank determinations (using water, 1.00 ml., instead of the solution of the nitrogenous substance) should be carried out simultaneously.

Distillation.

The decomposition of the ammonium salt [1] and distillation of the ammonia is carried out in the apparatus illustrated in Fig. 7, 1. This

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[1] If the method is used for the determination of ammonia in an ammonium salt, digestion is unnecessary. The solution of the ammonium salt is introduced into the flask F and made alkaline with 40% alkali ; the subsequent procedure is as above.

consists essentially of a long-necked flask F, with inlet and outlet tubes (I and O) and a condenser C. The head (carrying the tubes I and O) is fitted into F by a ground-glass joint J. Steam is passed from a generator through a trap (to remove condensed water; not illustrated) into the flask through I. It passes out through O and is condensed in C; the water formed is collected in a flask T. Before the apparatus is used steam is passed through it for 10 minutes to remove any ammonia present. The steam supply is disconnected, the head removed from the flask and the digested mixture (prepared as described in the preceding paragraph) washed into the flask F quantitatively with water (total volume about 15 ml.). The head is replaced and tube O connected to the condenser. Standard sulphuric acid (approximately 0·1N, 10·00 ml.) and methyl red-methylene blue indicator (5 drops) are placed in the flask T, which is fixed so that the lower end of the condenser L is *just* below the surface of the liquid.

A small funnel is attached with rubber tubing to I, and sodium hydroxide (40% aqueous solution, 10 ml.) is poured into F through this. The funnel is removed and the steam supply immediately attached to I. A rapid current of steam is passed through the apparatus for 10 minutes. At the end of this time, T is lowered so that L is above the surface of the acid, and steam is passed for 2 minutes more. The steam supply is now disconnected from I and the outside of L washed down with water.
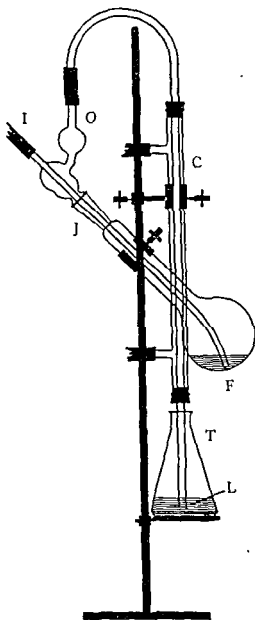
FIG. 7, 1
Micro-Kjeldahl Apparatus

Titration.

The excess acid in T is titrated with standard sodium hydroxide solution (approximately 0.1N), which should be carbonate-free. The end-point is the colour change, violet—*dull bluish grey*—green.
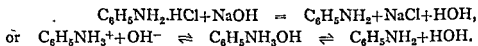
Calculation.

The amount of acid neutralised by the liberated ammonia is calculated by the usual method for a back titration (p. 137). The weight of nitrogen in the original sample is then calculated from the equation :

$$1.00 \text{ ml. } 1\text{N acid} = 1.00 \text{ ml. } 1\text{N-NH}_3 = 14.0 \text{ mg. nitrogen.}$$

7, 22   DETERMINATION OF THE EQUIVALENT OF A BASE

The equivalent of a base, which is a solid soluble in water, may be determined by means of a standard strong-acid solution, just as the equivalent of an acid may be determined by means of a standard strong-base solution (see Section 7, 19, pp. 144–145).

Many weak organic bases are sparingly soluble in water. Their strong-acid salts (chlorides, sulphates or nitrates) are usually soluble in water and are hydrolysed in solution, reacting acid. They may be titrated as acids with strong-base solutions (just as weak-acid strong-base salts like sodium carbonate or borax may be titrated as bases with a strong acid). Consider, for example, the titration of aniline hydrochloride with sodium hydroxide.

$$C_6H_5NH_2.HCl + NaOH \rightleftharpoons C_6H_5NH_2 + NaCl + HOH,$$
$$\text{or } C_6H_5NH_3^+ + OH^- \rightleftharpoons C_6H_5NH_3OH \rightleftharpoons C_6H_5NH_2 + HOH.$$

At the end-point the solution contains sodium chloride and aniline, the hydrate of which, $C_6H_5NH_3OH$, is slightly dissociated ; the pH of the solution is therefore above 7 and an indicator of high pK value is required.

The titration of such a salt may be used to determine its equivalent and thence the equivalent of the base as follows :

Principle. A sample of the salt is weighed accurately, dissolved in water and the solution made up to a known volume in a graduated flask. The concentration of this solution in g. per litre is known accurately. The normality of the solution is determined by titration with standard solution of a strong acid, and the gram-equivalent of the salt calculated from the equation :

Concentration (in g. per litre) = Normality × Gram-Equivalent.

The gram-equivalent of the base may be obtained by subtracting

from the gram-equivalent of the salt the gram-equivalent of the acid present in the salt, *e.g.*,

$$C_6H_5.NH_2,HCl - HCl = C_6H_5NH_2.$$
$$\quad\quad Salt \quad\quad\quad Acid \quad\quad\quad Base$$
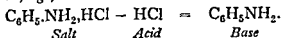
Gram-equivalents, 129·5 — 36·5 = 93·

Standard Solution. Sodium or potassium hydroxide (approximately 0·1N).

Unknown Solution. Solution of the weak-base strong-acid salt (prepared as described on pp. 139–141 ; should be very approximately 0·1N).

Other Details. As in section 7, 18, p. 144.

PRECIPITATION TITRATIONS

7, 23   INTRODUCTION

Many reactions in solution in which very sparingly soluble (so-called "*insoluble*") salts are precipitated can be used for determining the concentration of one or other of the ions of the "insoluble" salt. For example, the precipitation of sparingly soluble silver chloride (AgCl) forms the basis of methods for the determination of Ag^+ ions or of Cl^- ions. The reaction is

$$Ag^+ + Cl^- = AgCl\downarrow.$$

The principle of all such determinations is that to a known volume of the solution containing one ion (*e.g.*, the Cl^- ion) a solution containing the other ion of the "insoluble" salt (*e.g.*, the Ag^+ ion) is added *until precipitation is complete*. The three methods described below depend on the precipitation of insoluble silver halides or thiocyanate.

EQUIVALENTS

The gram-equivalent of a salt in precipitation reactions is the weight of the salt formed from one gram-equivalent of the appropriate acid and one gram-equivalent of the appropriate base. For example,

1 gram-equivalent of sodium chloride (NaCl)   = 1 gram-molecule.
1 gram-equivalent of calcium chloride (CaCl$_2$)   = $\frac{1}{2}$ gram-molecule.
1 gram-equivalent of aluminium sulphate (Al$_2$(SO$_4$)$_3$) = $\frac{1}{6}$ gram-molecule.

INDICATORS

The indicators used in precipitation titrations depend for their effect on solubility product relationships. (See pp. 89–90.)

STANDARD SOLUTIONS

Silver nitrate, sodium chloride, or potassium chloride can be used to prepare standard solutions by direct weighing for the titrations con-

sidered here. Solutions of thiocyanates must be standardised against silver solutions.

7, 24 DETERMINATION OF HALIDE BY STANDARD SILVER SOLUTION

Equation for reaction. $Ag^+ + Hal^- = AgHal\downarrow$ (Hal = Cl, Br or I).

Standard solution. Silver nitrate (approximately 0·05N or 0·1N).

Unknown solution. Chloride, bromide, or iodide (approximately 0·05N or 0·1N). See limitations of method below.

Solution in burette. Silver solution.

Indicator. Potassium chromate solution (K_2CrO_4, 0·5N, 2 drops).

End-point. Pale yellow (with white ppt.)—*pale orange* or *pink* (with white ppt.).

The colour-change is due to formation of red silver chromate (Ag_2CrO_4) after all the halide has been precipitated.

Limitations of method. The method can be used only if (*a*) the halide solution is neutral, since silver chromate is *not* precipitated in acid solution, and (*b*) the halide solution contains no cation which gives a precipitate with chromates (*i.e.*, all inorganic cations other than sodium, potassium, ammonium, calcium, and magnesium must be absent).

Points to Note.

1. In this titration (and in the titration described in the next section) it is *not* (as in acid-base titrations) a matter of choice which solution is placed in the burette. The nature of the indicator makes it necessary to put the silver solution into the burette.

2. The method can be used equally well to determine silver by means of a standard halide solution.

3. The end-point is the *first* permanent appearance of an orange or pink colour, *not* the *mid-point* of the colour-change (see p. 89).

4. All titration-mixtures and unused silver solutions should be placed in residue bottles for recovery.

7, 25 DETERMINATION OF THIOCYANATE BY MEANS OF STANDARD SILVER SOLUTION

Equation for reaction. $Ag^+ + SCN^- = AgSCN\downarrow$. .

Standard solution. Silver nitrate (approximately 0·05N or 0·1N).

Unknown solution. Sodium, potassium, or ammonium thiocyanate (approximately 0·05N or 0·1N).

Solution in burette. Thiocyanate solution.

Indicator. Ferric salt (Solution of ferric alum K_2SO_4, $Fe_2(SO_4)_3$, $24H_2O$ in nitric acid. 1·0 ml. in each titration).

End-point. Colourless (with white ppt.)—*pink* (with white ppt.).

The colour-change is due to the formation of red complex ferri-thiocyante ions $[Fe(SCN)_6]^{---}$, when all silver has been precipitated.[1]

Method. To each 10·00 ml. portion of silver nitrate solution add dilute nitric acid (5 ml.) before starting the titration. Shake vigorously during the addition of the thiocyanate solution.

Points to Note.

See preceding section.

7, 26   DETERMINATION OF HALIDE BY MEANS OF STANDARD SILVER AND THIOCYANATE SOLUTIONS

Principle. Back Titration (see pp. 136-137). The halide solution is acidified and treated with an *excess* of silver solution, which precipitates silver halide quantitatively. The excess of silver is then determined by titration with thiocyanate. In the determination of chloride the silver chloride must be removed by filtration before the thiocyanate titration is carried out, since it reacts slowly with the red ferri-thiocyanate ions formed at the end-point, giving silver thiocyanate.

$$6AgCl+[Fe(SCN)_6]^{---} \;=\; 6AgSCN+Fe^{+++}+6Cl^-.$$
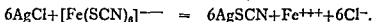
This reaction takes place because silver chloride is *more* soluble than silver thiocyanate. The end-point therefore fades slowly unless the silver chloride has been filtered off.

In the determination of bromide or iodide, the silver halide need not be filtered since these halides are *less* soluble than silver thiocyanate and therefore do not react with ferric thiocyanate.

This method (known as Volhard's method) is *not* subject to the limitations of the chromate-indicator method described on p. 150.

Equations for reactions.

    1. Precipitation of silver halide $Ag^+ + Hal^- \;=\; AgHal\downarrow$.
    2. Determination of excess silver $Ag^+ + SCN^- \;=\; AgSCN\downarrow$.
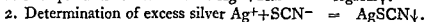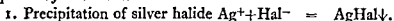
Standard solutions. Silver nitrate (approximately 0·1N). Sodium, potassium, or ammonium thiocyanate (approximately 0·05N).

Unknown solution. Solution of hydrochloric, hydrobromic, or hydriodic acid or of any chloride, bromide, or iodide (approximately 0·05N).

Method (for chloride). To the chloride solution (10·00 ml.) add dilute nitric acid (2N, 5 ml.) and standard silver solution (10·00 ml.). Shake the mixture to coagulate the precipitated silver chloride and

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[1] The red colour was formerly thought to be due to non-ionised ferric thiocyanate, $Fe(SCN)_3$.

sidered here. Solutions of thiocyanates must be standardised against silver solutions.

7, 24 DETERMINATION OF HALIDE BY STANDARD SILVER SOLUTION

Equation for reaction. $Ag^+ + Hal^- = AgHal \downarrow (Hal = Cl, Br \text{ or } I)$.

Standard solution. Silver nitrate (approximately $0.05N$ or $0.1N$).

Unknown solution. Chloride, bromide, or iodide (approximately $0.05N$ or $0.1N$). See limitations of method below.

Solution in burette. Silver solution.

Indicator. Potassium chromate solution (K_2CrO_4, $0.5N$, 2 drops).

End-point. Pale yellow (with white ppt.)—*pale orange* or *pink* (with white ppt.).

The colour-change is due to formation of red silver chromate (Ag_2CrO_4) after all the halide has been precipitated.

Limitations of method. The method can be used only if (*a*) the halide solution is neutral, since silver chromate is *not* precipitated in acid solution, and (*b*) the halide solution contains no cation which gives a precipitate with chromates (*i.e.*, all inorganic cations other than sodium, potassium, ammonium, calcium, and magnesium must be absent).

Points to Note.

1. In this titration (and in the titration described in the next section) it is *not* (as in acid-base titrations) a matter of choice which solution is placed in the burette. The nature of the indicator makes it necessary to put the silver solution into the burette.

2. The method can be used equally well to determine silver by means of a standard halide solution.

3. The end-point is the *first* permanent appearance of an orange or pink colour, *not* the *mid-point* of the colour-change (see p. 89).

4. All titration-mixtures and unused silver solutions should be placed in residue bottles for recovery.

7, 25 DETERMINATION OF THIOCYANATE BY MEANS OF STANDARD SILVER SOLUTION

Equation for reaction. $Ag^+ + SCN^- = AgSCN \downarrow$.

Standard solution. Silver nitrate (approximately $0.05N$ or $0.1N$).

Unknown solution. Sodium, potassium, or ammonium thiocyanate (approximately $0.05N$ or $0.1N$).

Solution in burette. Thiocyanate solution.

Indicator. Ferric salt (Solution of ferric alum K_2SO_4, $Fe_2(SO_4)_3$, $24H_2O$ in nitric acid. 1.0 ml. in each titration).

PERMANGANATE METHODS

Three volumetric determinations using permanganate in acid solution are described here, viz., the oxidation of ferrous to ferric salts, the oxidation of oxalic acid or oxalates to carbon dioxide and water, and the " mutual reduction " with hydrogen peroxide.

Dilute *sulphuric* acid is always used to acidify the reaction-mixture in these titrations, since it is neither an oxidising agent nor a reducing agent. Hydrochloric acid is unsuitable, since it is oxidised by permanganates. Nitric acid is unsuitable, being itself an oxidising agent.

Indicators.

Permanganate titrations are simpler than the acid-base titrations and precipitation titrations discussed previously in that *no* indicator need be added to the reaction-mixture. Solutions containing the permanganate ion are violet or pink, while solutions of its reduction products are almost colourless ; the appearance or disappearance of the pink colour therefore indicates the end-point of the reaction.

Standard Solutions.

The substances used for preparing standard solutions by direct weighing are sodium oxalate, arsenious oxide, oxalic acid, ferrous ammonium sulphate, and iron wire ; of these, sodium oxalate is the most satisfactory for elementary work.

Potassium permanganate cannot be used as a primary standard, because it is difficult to obtain perfectly pure and because ordinary distilled water contains traces of organic substances which reduce permanganate to manganese dioxide when the solution is made up. Permanganate solutions are therefore standardised against one of the above-mentioned substances.

IODINE METHODS

The only oxidation by iodine used here is the oxidation of thiosulphate to tetrathionate.

If the reaction between iodine and thiosulphates served only to determine these substances themselves, it would be of little importance. It can, however, be used for the volumetric determination of many *oxidising agents* which liberate from an iodide in solution quantities of iodine equivalent to themselves ; this iodine can then be determined by titration with thiosulphate.

Among the oxidising agents used in this way the following . . . .

Iodine is sparingly soluble in pure water, but readily soluble in aqueous solutions of potassium iodide. When iodine is liberated by an oxidising agent from potassium iodide, a considerable excess of the latter must be present in order to dissolve the liberated iodine.

filter it through a simple filter, collecting the filtrate in a conical flask. Wash out the reaction-flask six times with distilled water (about 5 ml. for each washing) from the jet of the wash-bottle, pouring the washings through the filter. Then wash the precipitate on the filter with distilled water (successive portions of about 5 ml. each) *until the washings are free from silver* (test with potassium iodide solution).

To the filtrate and washings add ferric alum indicator solution (2 ml.) and titrate with standard thiocyanate solution. Repeat the determination until titres agreeing within 0·10 ml. are obtained.

Method (for bromide and iodide). As for chloride except that the mixture of bromide (or iodide) solution, nitric acid, and silver solution is titrated with the thiocyanate solution without filtration.

OXIDATION-REDUCTION TITRATIONS

7, 27   **INTRODUCTION**

Many oxidation-reduction reactions in solution take place quantitatively and rapidly and may therefore be used for the volumetric determination of the substances taking part.

The principles of oxidation and reduction have been outlined with illustrative examples in Chapter 6 (pp. 112-118), to which reference should be made as necessary. The definitions of oxidation and reduction and of equivalents are repeated here.

The oxidation of a substance consists in (i) the *removal of electrons* from it, or (ii) an *increase* in the proportion of oxygen or other *electronegative* constituent in it, or (iii) a *decrease* in the proportion of hydrogen or other *electropositive* constituent in it.

The reduction of a substance consists in (i) the *addition of electrons* to it, or (ii) a *decrease* in the proportion of oxygen or other *electronegative* constituent in it, or (iii) an *increase* in the proportion of hydrogen or other *electropositive* constituent in it.

The *gram-equivalent* of any substance acting as an *oxidising agent* is the weight of the substance which oxidises 1·008 g. of hydrogen, or which contains 8·000 g. of oxygen available for oxidising purposes, or which absorbs one Faraday or "gram-equivalent" of electrons in the reaction.

The *gram-equivalent* of any substance acting as a *reducing agent* is the weight of the substance which contains 1·008 g. of hydrogen available for reducing purposes, or which requires 8·000 g. of oxygen to oxidise it, or which gives up one Faraday of electrons in the reaction.
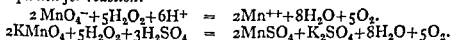
Two groups of oxidation-reduction titrations are treated here, viz., methods in which permanganate and iodine respectively are used as oxidising agents. The equivalents of potassium permanganate and iodine and the half-equations for their reduction have been considered on pp. 115-117.

2. Vessels which have contained permanganate solutions should be washed out as soon as possible after use. If the vessels are stained brown, they may be cleaned with warm bench dilute sulphuric acid to which a little oxalic acid has been added.

7, 29 DETERMINATION OF HYDROGEN PEROXIDE BY MEANS OF STANDARD PERMANGANATE

Principle. Potassium permanganate and hydrogen peroxide, both oxidising agents, liberate all their " available oxygen " as the element.
Equation for reaction.

$$2 MnO_4^- + 5H_2O_2 + 6H^+ = 2Mn^{++} + 8H_2O + 5O_2.$$
$$2KMnO_4 + 5H_2O_2 + 3H_2SO_4 = 2MnSO_4 + K_2SO_4 + 8H_2O + 5O_2.$$

" Half-equation " for the fate of the hydrogen peroxide

$$H_2O_2 = H_2O + (O).$$

Standard solution. Potassium permanganate (approximately 0·1N).
Unknown solution. Hydrogen peroxide (approximately 0·1N).
Solution in burette. Permanganate.
Indicator. None required.
End-point. Colourless—*pink*.
Method. Acidify the hydrogen peroxide solution (10·00 ml.) with sulphuric acid (about 20 ml., 2N), and titrate *cold*. Notes 1 and 2 in the preceding section apply here also.

" *Volume-strength* " *of hydrogen peroxide solutions.* The concentration of a hydrogen peroxide solution is often described in terms of " volume-strength," *i.e.*, the number of volumes of oxygen which can be obtained by the decomposition by heat of the hydrogen peroxide in one volume of the solution, $2H_2O_2 = 2H_2O + O_2$. For example, a " 10-volume " solution of hydrogen peroxide is a solution, 1 ml. of which will on decomposition evolve 10 ml. of oxygen.

If it is necessary to calculate the " volume-strength " of a solution of hydrogen peroxide from its concentration in grams per litre, the relation between the weight of " available oxygen " and its volume is supplied by the fact that one gram-molecular weight of any gas at N.T.P. occupies 22·4 litres.

7, 30 DETERMINATION OF FERROUS SALT BY MEANS OF STANDARD PERMANGANATE

Equation for reaction.

$$MnO_4^- + 5Fe^{+++} + 8H^+ = Mn^{++} + 5Fe^{+++} + 4H_2O, \text{ or}$$
$$2KMnO_4 + 10FeSO_4 + 8H_2SO_4 = 2MnSO_4 + K_2SO_4 + 5Fe_2(SO_4)_3 + 8H_2O.$$

[For deduction . . . . . .
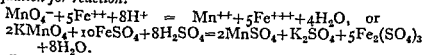
Un . . . . (approximately 0·1N).
Al . . . . ion of hydrogen peroxide (see preceding section).
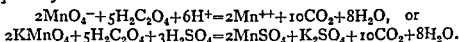
Indicator.

The iodide ion is colourless, whereas aqueous solutions containing free iodine are yellow or brown; however, the appearance or disappearance of the yellow colour of iodine serves only as a rough guide to the end-point in iodine-thiosulphate titrations. Iodine gives with *starch solution a blue colour far deeper than the yellow or brown* colour of the iodine itself, and the appearance or disappearance of this blue colour provides a much more sensitive test for the presence or absence of iodine in solution. Starch solution is therefore used as indicator in iodine titrations.

Standard Solutions.

Standard solutions of iodine can be prepared by direct weighing—although care must be taken if loss of iodine by volatilisation during the preparation is to be avoided. Sodium thiosulphate solutions are unstable, and therefore unsuitable for use as primary standards. Thiosulphate solutions are usually standardised against the iodine liberated from an excess of potassium iodide by a known amount of an oxidising agent (permanganate, dichromate, bromate, or iodate).

7, 28   STANDARDISATION OF PERMANGANATE BY MEANS OF OXALATE

Equation for reaction.

$$2MnO_4^- + 5H_2C_2O_4 + 6H^+ = 2Mn^{++} + 10CO_2 + 8H_2O, \quad \text{or}$$
$$2KMnO_4 + 5H_2C_2O_4 + 3H_2SO_4 = 2MnSO_4 + K_2SO_4 + 10CO_2 + 8H_2O.$$

The " half-equation " for the oxidation of oxalic acid is

$$H_2C_2O_4 - 2e = 2CO_2 + 2H^+ \quad \text{or} \quad H_2C_2O_4 + (O) = 2CO_2 + H_2O.$$
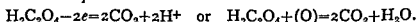
Standard solution. Sodium oxalate ($Na_2C_2O_4$, approximately 0·1N; prepared as sodium carbonate solution, see pp. 139–141).

Unknown solution. Potassium permanganate (approximately 0·1N).

Solution in burette. Permanganate.

Indicator. None required.

End-point. Colourless—*pink.*

Method. Take the sodium oxalate solution (10·00 ml.), acidify it with sulphuric acid (about 20 ml., 2N), add water (20 ml.) and heat to boiling. Titrate with the permanganate solution, running in the latter slowly at first. During the titration the temperature must be kept above 60°, and the pink colour must persist when the mixture is again heated to boiling.

Points to Note.

1. When measuring permanganate solution in a burette, read the level of the *top* of the meniscus instead of the level of the bottom, as is usual with other solutions.

The iodate method for the standardisation of thiosulphate solutions is an example of the converse use of these principles. Some other oxidising agents (as noted below) are also convenient for the standardisation of thiosulphate solutions.

1. Bromates.

The reaction is similar to that with iodate; reduction gives a bromide. The "half-equation" for the reduction of bromate is
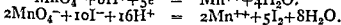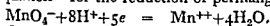
$$BrO_3^- + 6H^+ + 6e = Br^- + 3H_2O.$$
$$BrO_3^- + 6I^- + 6H^+ = Br^- + 3I_2 + 3H_2O.$$
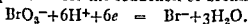
Potassium bromate is suitable for the standardisation of thiosulphate solutions.

2. Permanganates.

Reduction gives a manganous salt. The "half-equation" for the reduction of permanganate is

$$MnO_4^- + 8H^+ + 5e = Mn^{++} + 4H_2O.$$
$$2MnO_4^- + 10I^- + 16H^+ = 2Mn^{++} + 5I_2 + 8H_2O.$$

Allow five minutes for the permanganate-iodide reaction to take place before titrating with thiosulphate. Permanganate solutions (standardised against sodium oxalate) are suitable for the standardisation of thiosulphate solutions.

3. Dichromates.

Reduction gives a chromic salt (pale green solution). The "half-equation" for the reduction of dichromate is

$$Cr_2O_7^{--} + 14H^+ + 6e = 2Cr^{+++} + 7H_2O.$$
$$Cr_2O_7^{--} + 6I^- + 14H^+ = 2Cr^{+++} + 3I_2 + 7H_2O.$$
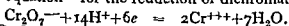
Allow five minutes for the dichromate-iodide reaction to take place before titrating with thiosulphate. To prevent atmospheric oxidation of hydriodic acid in the presence of chromic salt, pass a current of carbon dioxide through the reaction-flask during the whole process from the mixing of the dichromate, iodide, and acid solutions until the end of the titration.

Potassium dichromate is suitable for standardisation of thiosulphate solutions.

4. Cupric Salts.

Reduction gives a cuprous salt which is immediately precipitated as white cuprous iodide. The "half-equation" for the reduction of cupric ion is

$$Cu^{++} + e = Cu^+.$$
$$2Cu^{++} + 2I^- = 2Cu^+ + I_2.$$
$$2Cu^{++} + 2I^- = 2CuI\downarrow.$$
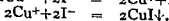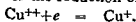
This reaction is carried out in neutral solution.

7, 31   STANDARDISATION OF THIOSULPHATE BY MEANS OF IODINE

Equation for reaction. $2S_2O_3^{--} + I_2 = S_4O_6^{--} + 2I^-$.
(For deduction see p. 115.)

Standard solution. Iodine (approximately 0·05N or 0·1N) in aqueous potassium iodide.

Unknown solution. Sodium thiosulphate (approximately 0·05N or 0·1N).

Solution in burette. Thiosulphate.

Indicator. Starch solution (1%). Add 0·5 ml. of this solution when the titration is *almost finished, i.e.,* when the brown colour of the iodine solution has been changed to a very pale yellow.

End-point. Blue—colourless.

7, 32   STANDARDISATION OF THIOSULPHATE BY MEANS OF IODATE

Principle. Iodates react quantitatively in acid solution with iodides liberating iodine, which is then titrated with thiosulphate as described in the preceding section.

Equations for reactions.

1. Liberation of iodine. $IO_3^- + 5I^- + 6H^+ = 3I_2 + 3H_2O$.

The "half-equation" for the reduction of iodate is
$$IO_3^- + 6H^+ + 5e = I + 3H_2O.$$
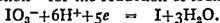
2. Titration. $I_2 + 2S_2O_3^{--} = S_4O_6^{--} + 2I^-$.

Standard solution. Potassium iodate (approximately 0·05N or 0·1N, prepared as sodium carbonate solution, see pp. 139–141).

Unknown solution. Sodium thiosulphate (approximately 0·05N or 0·1N).

Method. To the standard iodate solution (10·00 ml.) add potassium iodide solution (10%, 5 ml.) and dilute sulphuric acid (2N, 2 ml.). Titrate the liberated iodine with the thiosulphate solution, using starch indicator (see preceding section).

7, 33   DETERMINATION OF VARIOUS OXIDISING AGENTS BY MEANS OF STANDARD THIOSULPHATE

(Oxidising Agent) $+ 2xI^- \longrightarrow$ (Reduction products of oxidising agent) $+ xI_2$.

2. Titration. $xI_2 + 2xS_2O_3^{--} = xS_4O_6^{--} + 2xI^-$.

EXPERIMENTS IN PHYSICAL CHEMISTRY

The instructions for each experiment should be read in conjunction with the outline of the theory given in Chapter 6.

8, 1 PARTITION COEFFICIENTS

For theory see pp. 36-37.
This experiment shows the distribution of phthalic acid, a dibasic organic acid $C_6H_4(COOH)_2$, between water and ether.

Solubility of phthalic acid in water at $15°$ = 0.54 g. per 100 ml.

Solubility of phthalic acid in ether at $15°$ = 0.69 g. per 100 ml.

Partition coefficient $\dfrac{\text{ether}}{\text{water}}$ at $15°$ = $\dfrac{0.69}{0.54}$ = 1.28.

A 0.025M (0.050N) solution of phthalic acid in water (A) and a 0.025N solution of sodium hydroxide in water (B) are provided.

. . . . . . (50 ml).
an . . . . e water
into the ether. Allow the two layers to separate and run them off into different flasks. Titrate the aqueous solution (two 10.00 ml. portions, indicator, phenolphthalein) with the alkali solution B. Evaporate two 10.00 ml. portions of the ethereal solution separately to dryness in a distillation apparatus (p. 44), using a previously-warmed water bath. Dissolve the acid, which remains after the ether has evaporated, in warm water (approximately 10 ml.), cool and titrate with standard alkali solution B. Calculate the partition coefficient.

8, 2 RATE OF REACTION

For theory see p. 75.
Bromic acid and hydriodic acid react in aqueous solution according to the following equation:

$$HBrO_3 + 6HI = 3I_2 + HBr + 3H_2O.$$
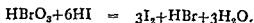
The rate of the reaction is directly proportional to the concentrations of bromic and hydriodic acids present. The rate is determined by measuring the time taken for the production of a given quantity of free iodine.

5. Chlorine or Bromine.

Reduction gives chloride or bromide ions.
The " half-equation " for the reduction is

$$Cl_2 + 2e = 2Cl^-.$$
$$Cl_2 + 2I^- = 2Cl^- + I_2.$$

This reaction is carried out in neutral or acidic solution.

6. Hypochlorites (including Bleaching Powder).

These on the addition of acid yield free chlorine which reacts with iodide as above. Bleaching powder reacts as follows :

$$Ca(OCl)Cl + 2H^+ = Cl_2 + H_2O + Ca^{++}.$$

FURTHER READING

VOGEL, A. I. A Text-Book of Quantitative Inorganic Analysis. Longmans, Green, London, 1944.

TREADWELL, F. P. Analytical Chemistry, Vol. II, Quantitative Analysis (Translated by HALL, W. T.), 8th edition. Wiley, New York, 1935.

CONWAY, E. J. Micro-Diffusion Analysis and Volumetric Error. Crosby Lockwood, London, 1939.
(This book deals very thoroughly with volumetric error, and with a special method of titration using volumes of about 0·1 ml.)

cyanate ions SCN⁻, and the deep red complex ferri-thiocyanate [Fe(SCN)₆]⁻⁻⁻ ions in aqueous solution.[1]

$$Fe^{+++} + 6SCN^- \ \rightleftharpoons\ [Fe(SCN)_6]^{---}$$
pale yellow   colourless   deep red
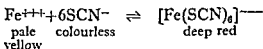
The following solutions are provided :

A . . Solution 0·005M in ferri-thiocyanate ions.
B . . Solution 0·1M in ferric ions.
C . . Solution 0·03M in thiocyanate ions.

In each of four boiling-tubes (I, II, III, IV) take solution A (10 ml.).
To tube I (control) add water (10 ml.).

To tube II add solution B (10 ml.) ; the red colour is much intensified, as the addition of ferric ions forces the equilibrium over in favour of the red complex ion.

To tube III add solution C (10 ml.) ; the red colour is again much intensified, as the addition of thiocyanate ions forces the equilibrium over in favour of the red complex ion.

To tube IV add mercuric chloride solution (0·1M, 10 ml.) ; the red colour is completely discharged. Mercuric chloride combine with free thiocyanate ions to give a colourless complex ; the removal of free thiocyanate forces the equilibrium over in favour of free ferric and thiocyanate ions, and all the complex ferri-thiocyanate ions dissociate

2. The Salting-Out Process.

This experiment illustrates the interference of a common ion with the equilibrium between a solid salt and its saturated aqueous solution Potassium chloride is precipitated from its solution by concentrated solutions of hydrochloric acid and potassium acetate, each of which provides a common ion.

$$K^+Cl^- \ \rightleftharpoons\ K^+ + Cl^-.$$
solid   in solution
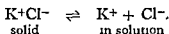
In each of two test-tubes I and II take potassium chloride solution (saturated, approximately 5M, 2·0 ml.). Add to the tubes respectively hydrochloric acid (" concentrated," approximately 11M, 2·0 ml.) and potassium acetate (saturated, approximately 25M, 2·0 ml.). In each tube a white crystalline precipitate of potassium chloride is formed.

3. Repression of the Ionisation of a Weak Electrolyte.

This experiment illustrates the repression of the ionisation of a weak electrolyte (ammonium hydroxide) by the addition of a strong electrolyte containing a common ion (ammonium chloride).
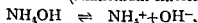
$$NH_4OH \ \rightleftharpoons\ NH_4^+ + OH^-.$$

[1] The red colour was formerly thought to be due to unionised ferric thiocyanate Fe(SCN)₃.

L

The following solutions are provided:

A. Potassium bromate . (0·08M).
B. Potassium iodide . (0·5M).
C. Acid+starch solution (0·1M hydrochloric acid containing starch 0·25 g. per litre).
D. Colour standard (Iodine 0·006 g., potassium iodide 0·02 g., starch 0·25 g. per litre.)

Take five beakers (50 ml. or 100 ml.), which should be of the same shape and made of the same glass. In one beaker place the colour standard D, 40 ml. Charge the other four beakers as shown below, adding the reagents in the order shown with stirring. In each case determine the *time* which elapses from the addition of solution B until the mixture reaches the same depth of colour as the standard D. The times range approximately from 50 to 200 seconds.

Beaker	I	II	III	IV
Solution C (ml.) .	40	40	40	40
Solution A (ml.) .	0·5	1·0	0·5	1·0
Solution B (ml.) .	0·5	0·5	1·0	1·0

If the initial concentrations of bromic and hydriodic acids in beaker I are x and y, the rate of reaction in this beaker will, according to the Law of Mass Action, be $r_1 = k.x.y$ (where k is a constant).

In the other beakers, the rates will be

$$r_2 = k.2x.y = 2r_1$$
$$r_3 = k.x.2y = 2r_1$$
$$r_4 = k.2x.2y = 4r_1.$$

Compare your results with those predicted by the Law of Mass Action.

8, 3   DYNAMIC EQUILIBRIUM

For theory see pp. 76 and 85-87. These experiments illustrate the *disturbance* of a dynamic equilibrium by the addition or removal of one of the substances taking part. The examples used here are all ionic equilibria, and most of them are examples of the common-ion effect.

1. Complex-Ion Formation.

The equilibrium studied is that between ferric ions Fe^{+++}, thio-

Five buffer solutions are provided, viz. :

A, $pH = 2$; B, $pH = 5$; C, $pH = 7$; D, $pH = 9$; E, $pH = 12$.

Three indicators are provided, viz. :

methyl red (M), red in acid, yellow in alkaline solution;
bromothymol blue (T), yellow in acid, blue in alkaline solution;
phenolphthalein (P), colourless in acid, pink in alkaline solution.

Examine the colours shown by these indicators in each of the five buffer solutions, using 1 ml. of the buffer solution and 1 drop of the indicator solution in each case. Set out your test-tubes in three rows of five, thus :

AM	BM	CM	DM	EM
AT	BT	CT	DT	ET
AP	BP	CP	DP	EP

Tabulate your results in the same way, and show your conclusions about the pH ranges of the indicators. Compare your findings with the data given on p. 164.

8, 6   DETERMINATION OF pH OF SOLUTIONS BY INDICATORS

For theory see pp. 98–100.

Solutions of unknown pH are provided, and the pH of each is to be determined by means of indicators, comparison being made with colour standards provided.

If the unknown solution is clear and colourless, use about 3 ml. of it and 3 drops of indicator. Compare colours by holding the unknown solution alongside the standard against a white background.

If the unknown solution is turbid and/or coloured (e.g., urine), the colour which is produced when the indicator is added to it must be compared with the standards in a comparator (or substitute) as described on p. 69. Use 5 ml. solution and 5 drops indicator in each case.

The pH of the unknown solution must first be determined roughly by means of Universal Indicator. This is a mixture of indicators which takes on the colours of the spectrum in order as the pH changes approximately as follows :

pH	Colour	pH	Colour
0–1	Deep red	8	Green
2–3	Red	9	Blue-green
4–5	Orange	9·5	Blue
6	Yellow	10·14	Violet-blue
7	Yellow-green		

(In the laboratory refer to the standards provided, *not* to this list. The naming of the colours is a matter of personal taste.)

Addition of much ammonium ion forces the equilibrium over in favour of undissociated ammonium hydroxide molecules.

This process is used in the usual cation separation in the precipitation of Group 3 to prevent the precipitation of metals of the later groups.

In each of two test-tubes (I and II) take ammonium hydroxide solution (0·1M, 5·0 ml.) and universal indicator (1 drop). Compare the colour with the standards and note the approximate *p*H of the solution. To tube I add water (1·0 ml.); no appreciable change in colour (or *p*H) occurs. To tube II add ammonium chloride (4M, 1·0 ml.). The colour changes to green, showing that the *p*H has been reduced, *i.e.*, [H⁺] has been increased and [OH⁻] decreased by the addition of the ammonium salt.

8, 4   INDEPENDENCE OF RADICALS IN THE REACTIONS OF SALTS

For theory see pp. 76–77.

This experiment illustrates the independence in the reactions of salts of the two parts of the salt molecule, formerly called *acidic* and *basic radicals*, and now called *anions* and *cations*.

Mix together in test-tubes in turn aqueous solutions of each of the five following salts, with aqueous solutions of each of the three following reagents :

Salts—mercuric chloride, mercuric sulphate, mercuric nitrate, magnesium chloride, sodium chloride (2 ml. each).

Reagents—sodium hydroxide (2 ml.), hydrogen sulphide (10 ml.), silver nitrate (2 ml.).

Tabulate your results and then answer the following questions in your note-book :

Which of the substances react in the same way with *sodium hydroxide* solution ?   What is common to all these substances ? .

Which substances react in the same way with *hydrogen sulphide* solution ?   What is common to all these substances ?

Which substances react in the same way with *silver nitrate* solution ? What is common to all these substances ?

Which reagents appear suitable for testing for mercuric salts ?

Which reagents appear suitable for testing for chlorides ?

After the practical class, study the chemistry of the reactions concerned in the sections on mercuric ion (p. 206) and chloride ion (p. 260).

8, 5   BEHAVIOUR OF INDICATORS

For theory see pp. 98–100.

The purpose of this experiment is to show that different acid-base indicators change colour over different *p*H ranges—or, in more colloquial language, have different ideas as to what is acid, neutral or alkaline.

Preparation of Solutions.

o·1M Hydrochloric acid solution and o·1M acetic acid solution are provided. From the o·1M hydrochloric acid solution prepare o·01M, o·001M, and o·0001M solutions as follows. In each of three test-tubes place 9·0 ml. water. To the first tube add 1·0 ml. o·1M hydrochloric acid from your graduated pipette and mix. This gives o·01M hydrochloric acid. Rinse the pipette three times with small volumes of this solution, returning them to the tube each time. Transfer 1·0 ml. of this o·01M hydrochloric acid to the second tube and mix. This gives o·001M hydrochloric acid. Rinse out the pipette with this solution. Then transfer 1·0 ml. of this solution to the third tube and mix. This gives o·0001M hydrochloric acid.

Prepare from the o·1M acetic acid solution similarly o·01M, o·001M, and o·0001M solutions of acetic acid.

Determination of pH Values.

Take in separate test-tubes approximately ·1 ml. of each of the eight solutions which you now have. Add to each tube 1 drop of methyl violet, shake, and compare with the colour standards.

Repeat these tests using 2 drops of bromophenol blue instead of 1 drop of methyl violet, and compare with the colour-standards.

Results.

Deduce from the colours obtained in these two series of tests the approximate *p*H value of each of the eight solutions. Tabulate the results in your note-book and compare them with the *p*H values calculated from equations (16) and (18), p. 94.

Note from the methyl violet series of tubes that o·001M hydrochloric acid has the same hydrogen-ion concentration as o·1M acetic acid, which is therefore about 1 per cent. ionised in o·1M solution.

Note from the bromophenol blue series of tubes that while tenfold dilution of hydrochloric acid (from o·001M to o·0001M) produces an increase in *p*H of 1, hundred-fold dilution of acetic acid (from o·1M to o·001M) is necessary to produce an equal increase in *p*H.

8, 8   SALT HYDROLYSIS

For theory see pp. 95–96.

Determine by means of indicators the *p*H values of o·1M solutions of the following salts, and compare the results obtained with those calculated from equations (24) (27) and (29) on pp. 95–96.

Sodium chloride (strong acid ; strong base).
Sodium acetate (weak acid, pK_a=4·75 ; strong base).
Ammonium chloride (strong acid ; weak base, pK_b=4·75).
Ammonium acetate (weak acid ; weak base).

Wl

thus,

range

mination (to the nearest 0·5 pH unit). Standards are provided showing the colours of these indicators at intervals of 0·5 pH unit over their useful ranges.

Indicator	pK	Colours and Useful pH Range
Methyl violet	..	Yellow (fades) 0·0, green (fades) 1·0, blue 2·0, violet 3·0.
Thymol blue (first change)	1·7	Red 1·2- 2·8 yellow.
Bromophenol blue [1]	4·0	Yellow 3·0- 4·6 violet.
Bromocresol green	4·7	Yellow 3·8- 5·4 blue.
Methyl red	5·1	Red 4·3- 6·1 yellow.
Bromocresol purple	6·3	Yellow 5·2- 6·8 purple.
Bromothymol blue [2]	7·0	Yellow 6·0- 7·6 blue.
Phenol red	7·9	Yellow 6·8- 8·4 red.
Thymol blue (second change)	8·9	Yellow 8·0- 9·6 blue.
Phenolphthalein	9·7	Colourless 8·2-10·0 pink.

8, 7   STRENGTH OF ACIDS. BEHAVIOUR OF ACIDS ON DILUTION

For theory see pp. 93–95.

The purposes of this experiment are (1) to show the difference in degree of ionisation between strong and weak acids at equal molar concentrations, and (2) to illustrate the difference in behaviour of strong and weak acids on dilution. The pH values of a strong acid and a weak acid at different dilutions are determined by means of indicators.

Hydrochloric acid is used as an example of a strong acid (completely ionised at the dilutions used here) and acetic acid as an example of a weak acid (pK_a=4·75). No single indicator covers the required pH range completely; two indicators are therefore used, viz.: methyl violet—yellow at pH 0·0, green at pH 1·0, blue at pH 2·0, violet at pH 3·0 and above—and bromophenol blue—yellow at pH 3·0 and below, dull brown at pH 3·5, violet at pH 4·0 and above. Standards showing these colours are provided in the laboratory.

[1] Methyl orange (pK = 3·7, useful range pH 3·1–4·4, red-yellow) is widely used, but is less satisfactory than bromophenol blue because its colour-change is less sharp.

The end-point ⟨   of a blue dyestuff on the pH of the s alkaline solution⟩

[2] Litmus is a mixture of substances which changes colour from red to blue over the pH range 5–8. It is now used only for rough qualitative work.

in pH which take place in tubes I and III, using equation (31) and assuming that *all* added H+ or OH− ions are " mopped up " as shown on pp. 97-98.

8, 10   TITRATION CURVE

For theory see pp. 103-106.

.   .   .   .   cid-base titration may be
.   .   .   .   .   .   reaction-mixture by means
.   the burette.

The titration of phosphoric acid (H_3PO_4) with sodium hydroxide is a convenient example. The indicators to be used are :

1. *Methyl Violet*—determines the initial pH of phosphoric acid.

2. *Bromocresol Green*—changes colour sharply at the point where NaH_2PO_4 is formed.

3. *Bromothymol Blue*—changes colour slowly over the buffer range of primary phosphate secondary phosphate mixtures.

4. *Phenolphthalein*—changes colour sharply at the point where Na_2HPO_4 is formed.

Solutions of phosphoric acid and sodium hydroxide (each 0·100M) are provided. Take four 10·00 ml. portions of the phosphoric acid (I, II, III, IV) and dilute each to 100 ml. with water.

Determine the pH of portion I (after dilution) with methyl violet.

Titrate portions II, III, and IV (after dilution) with the standard sodium hydroxide, using the indicators listed below. Determine the pH of each reaction-mixture after the stated volumes of alkali have been added, by comparison with the colour standards provided.

Portion II. Bromocresol Green. 9·50, 9·80, 9·90, 10·00, 10·10, 10·20, 10·50 ml.

Portion III. Bromothymol Blue. 11·00, 12·00, 13·00, 14·00, 15·00, 16·00, 17·00, 18·00, 19 00 ml.

Portion IV. Phenolphthalein. 19·50, 19·80, 19·90, 20·00, 20·10, 20·20, 20·50 ml.

Construct from your results a titration curve, and compare it with that determined potentiometrically and shown on p. 103.

8, 11   COMPETITION OF TWO ACIDS FOR ONE BASE

For theory see p. 108.

The following examples illustrate fair and unfair competition of two acids for one base.

8, 9   BUFFER SOLUTIONS

For theory see pp. 96-98.

The purpose of these experiments is to illustrate the resistance of a buffer solution to change of *p*H (1) on dilution and (2) on the addition of acid or alkali.

DILUTION

An acetic acid sodium acetate buffer solution (B) of *p*H 4·75 is provided. Take 1·0 ml. of this buffer, add it to 9·0 ml. distilled water and mix thoroughly. Call this solution B/10. Wash the pipette out with this solution as described on p. 165. Take 1·0 ml. of B/10, add it to 9·0 ml. distilled water and mix thoroughly. Call the solution so obtained B/100. In separate test-tubes take 1 ml. of each of the solutions B, B/10, B/100; add to each 2 drops of bromocresol green, shake, and compare the colours with the standards.

Note that the colours (and hence the pH values of the solutions) in the three tubes are almost identical. The pH of a buffer solution is unchanged by dilution.

EFFECT OF ADDING ACID OR ALKALI

Acid and alkali are added in turn to a buffer solution, and to water, and the changes in *p*H compared. An acetate buffer solution of *p*H 4·75 will be used as in the previous experiment.

Label six test-tubes I, II, III, IV, V, VI. Charge them as follows, adding the reagents in the order stated:

Tube	I	II	III	IV	V	VI
Buffer solution (ml.)	5·0	5·0	5·0	0	0	0
Water ,,	0	0	0	5·0	5·0	5·0
Bromocresol green* (drops)	2	2	2	2	2	2
0·1 M-HCl solution (ml.)	5·0†	0	0	0·05‡	0	0
0·1 M-NaOH solution ,,	0	0	5·0†	0	0	0·05‡
Water ,,	0	5·0	0	0	0	0

* Mix the contents of each tube and note the colour before proceeding.
† Add these volumes slowly from a burette.
‡ One drop.

Tubes II and V are controls. Compare the colours produced in the tubes with the standards and draw your conclusions. Tabulate the account of your work in your note-book in the above form.

The acetate buffer solution contains 0·50 g.-mols. acetic acid per litre and 0·50 g.-mols. sodium acetate per litre. Work out the changes

in pH which take place in tubes I and III, using equation (31) and assuming that *all* added H$^+$ or OH$^-$ ions are " mopped up " as shown on pp. 97–98.

8, 10 TITRATION CURVE

For theory see pp. 103–106.

An approximate titration curve for an acid-base titration may be obtained by determining the pH value of the reaction-mixture by means of indicators, after successive additions from the burette.

The titration of phosphoric acid (H$_3$PO$_4$) with sodium hydroxide is a convenient example. The indicators to be used are :

1. *Methyl Violet*—determines the initial pH of phosphoric acid.

2. *Bromocresol Green*—changes colour sharply at the point where NaH$_2$PO$_4$ is formed.

3. *Bromothymol Blue*—changes colour slowly over the buffer range of primary phosphate secondary phosphate mixtures.

4. *Phenolphthalein*—changes colour sharply at the point where Na$_2$HPO$_4$ is formed.

Solutions of phosphoric acid and sodium hydroxide (each 0·100M) are provided. Take four 10·00 ml. portions of the phosphoric acid (I, II, III, IV) and dilute each to 100 ml. with water.

Determine the pH of portion I (after dilution) with methyl violet.

Titrate portions II, III, and IV (after dilution) with the standard sodium hydroxide, using the indicators listed below. Determine the pH of each reaction-mixture after the stated volumes of alkali have been added, by comparison with the colour standards provided.

Portion II. Bromocresol Green. 9·50, 9 80, 9·90, 10·00, 10·10, 10·20, 10·50 ml.

Portion III. Bromothymol Blue. 11·00, 12·00, 13·00, 14·00, 15·00, 16·00, 17·00, 18·00, 19·00 ml.

Portion IV. Phenolphthalein. 19·50, 19·80, 19·90, 20·00, 20·10, 20·20, 20·50 ml.

Construct from your results a titration curve, and compare it with that determined potentiometrically and shown on p. 103.

8, 11 COMPETITION OF TWO ACIDS FOR ONE BASE

For theory see p. 108.

The following examples illustrate fair and unfair competition of two acids for one base.

FAIR COMPETITION

1. *Displacement of Weak Acid by Strong Acid.*

Dissolve sodium acetate (2 spatula-points) in water (2 ml.). The solution has no smell. Add dilute sulphuric acid (2 ml.) and shake. The smell of acetic acid is perceptible.

2. *Displacement of Weak Acid by Strong Acid. "Solution" of Insoluble Salt.*

To calcium phosphate, $Ca_3(PO_4)_2$ (2 spatula-points), add water (2 ml.); the salt is insoluble.

To calcium phosphate (2 spatula-points) add dilute hydrochloric acid (2 ml.); the salt "dissolves" due to the formation of unionised phosphoric acid by phosphate ions and the added hydrogen ions.

Reduce the hydrogen-ion concentration of the solution by adding dilute ammonia dropwise. Calcium phosphate is re-precipitated.

UNFAIR COMPETITION

3. *Displacement of Weak Volatile Acid by Strong Non-Volatile Acid.*

To sodium sulphide (aqueous solution, 2 ml.) add dilute sulphuric acid (2 ml.). Hydrogen sulphide is evolved as a gas.

4. *Displacement of Weak Sparingly Soluble Acid by Strong Soluble Acid.*

To sodium benzoate ($C_6H_5.COONa$, aqueous solution, 2 ml.) add dilute sulphuric acid (2 ml.). Benzoic acid ($C_6H_5.COOH$) is precipitated.

5. *Displacement by Weak Unstable Acid by Strong Stable Acid.*

To sodium carbonate solution (2 ml.) add dilute sulphuric acid (2 ml.). Carbonic acid is formed by displacement and decomposes, giving carbon dioxide, which is evolved as a gas.

6. *Displacement by Strong Volatile Acid by Weak Non-Volatile Acid.*

To sodium chloride (aqueous solution, 2 ml.) add dilute phosphoric acid (2 ml.) and heat. Hydrochloric acid is evolved as a gas, because, although much stronger than phosphoric acid, it is volatile and cannot fairly compete with the latter.

8, 12   DEPRESSION OF THE FREEZING-POINT

For theory see p. 119.

The purpose of this experiment is to demonstrate the depression of the freezing-point of a solvent by a solute, and the difference in behaviour between non-electrolytes and electrolytes.

The apparatus used is illustrated in Fig. 8, 1. The inner tube A contains the liquid whose freezing-point is to be measured; the thermometer T (range −10 to 50°, graduated in $\frac{1}{5}$°) and the stirrer S (made of copper wire) are held in place by a two-hole stopper. The outer tube B serves as an air jacket. Aqueous solutions (each 1·0M) of urea (CO(NH₂)₂), non-electrolyte) and of sodium chloride (NaCl, strong electrolyte) are provided.

Fill a beaker (600 ml. to 1000 ml.) with an ice-salt freezing-mixture, adjusting the proportions so that the temperature is −5° or −6°. Place water (10 ml.) in the tube A, insert the cork, thermometer and stirrer, and hold the tube in the bath until solidification begins. Wipe the outside of A, and fit it into the outer tube B; then place the whole apparatus in the freezing-mixture and stir until the temperature shown by the thermometer is constant. Record this temperature to the nearest $\frac{1}{10}$°.

Dismantle the apparatus and determine, in the same way, the freezing-points of the urea and sodium chloride solutions. Calculate the freezing-point depressions, and note that 1·0M sodium chloride gives approximately *twice* the depression given by 1·0M urea.

Many other determinations of freezing-point depressions may be carried out with this apparatus.

1. Comparison of 0·5M, 1·0M, 1·5M, 2·0M solutions of urea.

2. Comparison of 1·0M urea, glucose, acetamide (all non-electrolytes).

3. Comparison of 1·0M hydrochloric acid (strong electrolyte) and acetic acid (weak electrolyte).

4. Comparison of 1·0M solutions of strong electrolytes giving rise to different numbers of ions, *e.g.*, sodium chloride (NaCl, gives 2 ions), calcium chloride (CaCl₂, gives 3 ions), aluminium chloride (AlCl₃, gives 4 ions).
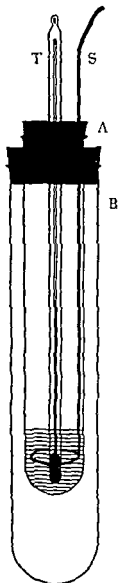
FIG. 8, 1

Freezing-Point Apparatus

8, 13   ADSORPTION

For theory see p. 121.

The purpose of this experiment is to demonstrate the adsorption of a solute (acetic acid) by a finely divided solid (charcoal).

Measure acetic acid (0·500N solution, 50·0 ml.) with a measuring cylinder into a conical flask. Add charcoal (1·0 g.), shake and allow to settle. When the charcoal has settled, pipette off two 10·00 ml. portions of the supernatant liquid and titrate with standard sodium hydroxide (0·100N). Calculate the normality of acetic acid in the supernatant liquid. Note that this is *less than* 0·500N (since some acetic acid has been adsorbed by the charcoal).

8, 14   EMULSIFICATION

For theory see p. 122.

The purpose of this experiment is to show how a water-insoluble oil may be dispersed as an emulsion in water with the aid of emulsifying agents such as soaps.

In each of three test-tubes (I, II, III) take triolein (1 drop). To tube I add water (5 ml.) and shake vigorously; triolein does not dissolve or form an emulsion, but floats on the water as a globule. To tubes II and III add aqueous solutions of sodium oleate and cetyltrimethylammonium bromide (0·1%, 5 ml. each) respectively, and shake vigorously; in each case a stable cloudy emulsion of triolein in water is formed.

8, 15   PARTICLE SIZE

For theory see p. 123.

The particles of substances in suspension, in colloidal solution and in true solution differ in size. On account of the differences in particle-size, substances in these three conditions can be separated by filter-paper and by dialysing membranes (*e.g.*, parchment-paper), as illustrated in the following experiments:

1. Three blue substances are provided, viz. :

Indigo (in suspension in water);
Prussian blue (in colloidal solution in water); and
Copper sulphate (in true solution in water).

Fit filter-papers into three small funnels, and pour into the papers respectively 10 ml. of each of the three materials mentioned. The material in suspension (indigo) does *not* pass through the filter-paper; the materials in colloidal solution and in true solution do pass.

Fold two circles of parchment-paper in quarters, open them into cones like filter-papers, and fix each separately into this shape with paper-fasteners. Almost fill two small beakers with distilled water and rest the cones of parchment-paper on top of the beakers. Place in the cones respectively the colloidal solution of Prussian blue (beaker I) and the true solution of copper sulphate (beaker II) (10 ml. of each) and leave for two hours. At the end of this time the liquid

outside the parchment-paper in beaker II will be blue—*i.e.*, copper sulphate will have dialysed out; the liquid outside the parchment in beaker I will not be blue, *i.e.*, Prussian blue will *not* have dialysed out.

2. An aqueous solution containing sodium chloride (in true solution) and starch (in colloidal solution) is provided. Place this solution (10 ml.) in a parchment cone in a beaker of water (as described in experiment 1 above). Test the liquid in the cone and that in the beaker *immediately* for starch and for chloride.[1] Repeat the tests on each liquid one hour afterwards. Leave the apparatus to stand for a week, replacing the liquid in the beaker with fresh distilled water three times during the interval. Test the liquid in the cone and that in the beaker for starch and for chloride [1] at the end of the week. Tabulate your results.

8, 16   LYOPHILIC AND LYOPHOBIC SOLS

For theory see pp. 124–127.

COAGULATION AND REVERSIBILITY OF SOLS

Lyophilic sols are not coagulated by traces of electrolytes; they are coagulated by high concentrations of electrolytes; they are brought back into colloidal solution by the addition of more water.

Lyophobic sols are coagulated by traces of electrolytes; they are not brought back into colloidal solution by the addition of more water.

The examples used are gelatin (lyophilic) and arsenious sulphide (*POISONOUS*, lyophobic).

Effect of Traces of Electrolytes.

Take in separate boiling-tubes the gelatin sol and the arsenious sulphide sol (5 ml. each). To each tube add slowly and with shaking calcium chloride solution (0·01M, 2·5 ml.). The arsenious sulphide is completely precipitated, while the gelatin is not affected. Now add to the arsenious sulphide tube water (15 ml.); the precipitate is *not* redissolved.

Effect of High Concentrations of Electrolytes.

Take in separate boiling-tubes the gelatin sol and the arsenious sulphide sol (5 ml. each). To each tube add ammonium sulphate solution (saturated, 5 ml.). Both arsenious sulphide and gelatin are precipitated. Now add to each tube water (15 ml.); the gelatin redissolves, the arsenious sulphide does *not*.

[1] Take 1 ml. of each solution for each test. Test for starch by means of a dilute solution of iodine in aqueous potassium iodide, and for chloride by means of aqueous silver nitrate solution.

CO-PRECIPITATION OF OPPOSITELY-CHARGED LYOPHOBIC SOLS

Arsenious sulphide sols (negatively charged) and ferric hydroxide sols (positively charged) precipitate one another if mixed in the appropriate quantities.

In each of five test-tubes take the given arsenious sulphide sol (5·0 ml.). To these tubes add the given ferric hydroxide sol (0·1, 0·2, 0·5, 1·0, 2·0 ml. respectively). Mix the contents of each tube thoroughly, and allow the tubes to stand for half an hour. Then note the appearance of the mixtures and draw your conclusions. Tabulate your results.

PROTECTION OF LYOPHOBIC SOL BY LYOPHILIC SOL

Arsenious sulphide (lyophobic sol) is protected by starch (lyophilic sol).

In each of two test-tubes take arsenious sulphide sol (5 ml.). To one tube add water (5 ml.) followed by 0·5M ammonium sulphate solution (1 ml.). To the other tube add a starch sol (1%, 5 ml.) followed by 0·5M ammonium sulphate solution (5 ml.). Compare the results of the two tests.

8, 17   **GELS**

For theory see p. 127.

This experiment illustrates the reversible sol-gel transformation.

A tube is provided containing a gelatin-in-water gel (5%, about 3 ml.). At room temperature this gel looks like a solid. Heat the tube in your water bath until the gel liquefies, then cool it to room temperature and set it aside. The liquid gels again.

FURTHER READING

THEORETICAL TEXT-BOOKS

See the list on p. 128.

PRACTICAL TEXT-BOOKS

FINDLAY, A. Practical Physical Chemistry, 6th edition. Longmans, Green, London, 1935.

KERRIDGE, P. M. T. Principles of Physical Chemistry for Medical Students. Oxford University Press, London, 1927.

INORGANIC CHEMISTRY

REACTIONS OF COMMON INORGANIC SUBSTANCES

9, 1   INTRODUCTION

This chapter outlines those reactions of the commoner elements and their compounds which can be carried out in an elementary course. Many important reactions must be omitted since they cannot conveniently be done by students themselves. The elements and their compounds are classified according to the Periodic Table (see p. 79). A secondary purpose of this chapter is to provide the information upon which a scheme for the identification of simple inorganic substances may be built. The bulk of this chapter (a hundred-odd pages) may perhaps frighten students ; the author feels, however, that this full treatment is necessary if practical inorganic chemistry is to be something more than rule-of-thumb qualitative analysis. Many instructors will probably omit some of the less common metals (e.g., cadmium, cobalt, nickel).

An analysis scheme, restricted in scope, is outlined in chapter 10 (pp. 278-293). Most tests in inorganic qualitative analysis are carried out on aqueous solutions prepared from the substances provided for analysis ; the solutions contain the *ions* of which the original substances are composed, or *related ions* into which they have been transformed. Inorganic qualitative analysis is therefore largely a matter of the recognition of ions, and a majority of the tests used involve the combination of ions to form a precipitate of an insoluble substance. Since these ionic reactions are most convenient for elementary laboratory work and since qualitative analysis provides excellent practice in logical deduction, many courses include little inorganic chemistry besides the recognition of simple salts. The author does not claim to have avoided this tendency entirely, but hopes that sufficient reactions other than simple ionic reactions have been included to prevent the student from thinking that only the latter are important. It has been pointed out that no test is of value for recognition purposes, unless the behaviour in that test of *every* substance likely to be present has been studied. This principle has been followed in preparing the sections in this chapter which deal with anions and cations included in the scheme of analysis. For each test used, the behaviour of every ion, which could be present when that test is applied, is mentioned in the appropriate section.

CO-PRECIPITATION OF OPPOSITELY-CHARGED LYOPHOBIC SOLS

Arsenious sulphide sols (negatively charged) and ferric hydroxide sols (positively charged) precipitate one another if mixed in the appropriate quantities.

In each of five test-tubes take the given arsenious sulphide sol (5·0 ml.). To these tubes add the given ferric hydroxide sol (0·1, 0·2, 0·5, 1·0, 2·0 ml. respectively). Mix the contents of each tube thoroughly, and allow the tubes to stand for half an hour. Then note the appearance of the mixtures and draw your conclusions. Tabulate your results.

PROTECTION OF LYOPHOBIC SOL BY LYOPHILIC SOL

Arsenious sulphide sol (lyophobic sol) is protected by starch (lyophilic sol).

In each of two test-tubes take arsenious sulphide sol (5 ml.). To one tube add water (5 ml.) followed by 0·5M ammonium sulphate solution (1 ml.). To the other tube add a starch sol (1%, 5 ml.) followed by 0·5M ammonium sulphate solution (5 ml.). Compare the results of the two tests.

8, 17   **GELS**

For theory see p. 127.

This experiment illustrates the reversible sol-gel transformation.

A tube is provided containing a gelatin-in-water gel (5%, about 3 ml.). At room temperature this gel looks like a solid. Heat the tube in your water bath until the gel liquefies, then cool it to room temperature and set it aside. The liquid gels again.

FURTHER READING

THEORETICAL TEXT-BOOKS

See the list on p. 128.

PRACTICAL TEXT-BOOKS

FINDLAY, A. Practical Physical Chemistry, 6th edition. Longmans, Green, London, 1935.

KERRIDGE, P. M. T. Principles of Physical Chemistry for Medical Students. Oxford University Press, London, 1927.

Instructors may in some cases arrange for students to do further examples of each class of reaction. It appears undesirable to make students carry out *all* the other reactions, even if time permits, since they will only be bored by long series of tests in which the visible results are virtually identical.

Many qualitative tests involve two or three successive stages (*e.g.*, formation of a precipitate "soluble" in excess of the reagent; charcoal block tests). These tests can only be understood if the individual processes are considered as separate reactions.

Each reaction is denoted in the lists by the symbol of the element under which it will be found, followed by a number, thus, *e.g.*, "Mg, 1".

OXIDATION-REDUCTION REACTIONS

For theory see pp. 112-118. The "dry" reactions (those taking place in the absence of water) and the "wet" reactions (those taking place in aqueous solution) are best considered by the "atomic" and "electronic" methods respectively.

Dry Reactions.

Burning of the following elements in air or oxygen to give oxides.

1. Magnesium	Mg, 1 .	p. 196
2. Calcium	Ca, 1 .	p. 198
3. Hydrogen	H, 2 .	p. 187
4. Carbon	C, 1 .	p. 212
5. Phosphorus	P, 1 .	p. 234
6. Sulphur	S, 1 .	p. 247

Other Combinations.

7. Iron and sulphur . .	S, 2 .	p. 247
8. Iron and chlorine . .	Cl, 2 .	p. 259
9. Phosphorus and bromine .	Br, 1 .	p. 262

Decompositions by Heat.

10. Mercuric oxide . .	Hg, 1 .	p. 205
11. Lead peroxide . .	Pb, 2 .	p. 225

Other Reductions.

12. Cupric oxide and carbon .	Cu, 3*a* .	p. 192
See also nos. 80 and 81.		

Wet Reactions.

Simple Losses and Gains of Electrons.

13. Calcium and water . .	Ca, 2 .	p. 198
14. Zinc and hydrochloric acid .	H, 1 .	p. 187

The reactions considered in this chapter fall into one or other of a few general types. The realisation of this fact will make inorganic chemistry, and particularly inorganic qualitative analysis, much easier to the student. Representative reactions to familiarise beginners with the most important types are listed in section 9, 2 (pp. 174–180). The importance of the solubilities of salts in water has been emphasised already (pp. 88–91), and a table of soluble and insoluble salts is given in section 9, 3 (p. 180).

To facilitate reference and to emphasise the value of an orderly treatment of a mass of data, the sections of this chapter dealing with the elements are arranged on a common plan, described in section 9, 4 (pp. 180–182). General instructions for laboratory work and a suggested form for students' reports of their work are given in sections 9, 5 and 9, 6 (pp. 183–186 and pp. 186–187) respectively.

The normal biological rôles of the inorganic ions have been briefly noted with particul . . . . inorganic ions play . . . . potassium, calcium, ... carbonate being the principal ones in mammals. Other elements, *e.g.*, zinc and copper, are essential in traces.

The medical uses of inorganic compounds are also mentioned. These uses may be classified as follows :

1. Substances which are normal body constituents (*e.g.*, calcium, iron, iodine) and which are administered to remedy deficiencies.

2. Substances not naturally present, for whose application a physico-chemical reason may be found, *e.g.*, saline purgatives, which act on account of osmotic effects, or astringents, which probably act by precipitating proteins.

3. Substances not naturally present, used on purely empirical grounds, *e.g.*, many mercury and arsenic compounds.

ABBREVIATIONS

The following are used in tables in this and subsequent chapters :

aq.	=	aqueous.
conc.	=	concentrated, concentration.
dec.	=	decomposes.
dil.	=	dilute.
insol.	=	insoluble.
O.S.	=	original solution.
ppt(d).	=	precipitate(d).
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9, 2 ## REPRESENTATIVE REACTIONS

The following selection illustrates most of the important general types of inorganic reactions, and should give students a " bird's-eye view " of inorganic chemistry.

Instructors may in some cases arrange for students to do further examples of each class of reaction. It appears undesirable to make students carry out *all* the other reactions, even if time permits, since they will only be bored by long series of tests in which the visible results are virtually identical.

Many qualitative tests involve two or three successive stages (*e.g.*, formation of a precipitate "soluble" in excess of the reagent; charcoal block tests). These tests can only be understood if the individual processes are considered as separate reactions.

Each reaction is denoted in the lists by the symbol of the element under which it will be found, followed by a number, thus, *e.g.*, "Mg, 1".

OXIDATION-REDUCTION REACTIONS

For theory see pp. 112-118. The "dry" reactions (those taking place in the absence of water) and the "wet" reactions (those taking place in aqueous solution) are best considered by the "atomic" and "electronic" methods respectively.

Dry Reactions.

Burning of the following elements in air or oxygen to give oxides.

1. Magnesium	. . . . .	Mg, 1	. . p. 196
2. Calcium	. . . . .	Ca, 1	. . p. 198
3. Hydrogen	. . . . .	H, 2	. . p. 187
4. Carbon	. . . . .	C, 1 .	. p. 212
5. Phosphorus	. . . . .	P, 1 .	. p. 234
6. Sulphur	. . . . .	S, 1 .	. p. 247

Other Combinations.

7. Iron and sulphur	. . .	S, 2 .	. p. 247
8. Iron and chlorine	. . .	Cl, 2	. . p. 259
9. Phosphorus and bromine	.	Br, 1	. . p. 262

Decompositions by Heat.

10. Mercuric oxide	. . .	Hg, 1	. . p. 205
11. Lead peroxide	. . .	Pb, 2	. . p. 225

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12. Cupric oxide and carbon	.	Cu, 3*a*	. p. 192

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Wet Reactions.

Simple Losses and Gains of Electrons.

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9, 2   **REPRESENTATIVE REACTIONS**

The following selection illustrates most of the important general types of inorganic reactions, and should give students a " bird's-eye view " of inorganic chemistry.

Instructors may in some cases arrange for students to do further examples of each class of reaction. It appears undesirable to make students carry out *all* the other reactions, even if time permits, since they will only be bored by long series of tests in which the visible results are virtually identical.

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Other Combinations.

7. Iron and sulphur	S, 2	p. 247
8. Iron and chlorine	Cl, 2	p. 259
9. Phosphorus and bromine	Br, 1	p. 262

Decompositions by Heat.

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Simple Losses and Gains of Electrons.

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The reactions considered in this chapter fall into one or other of a few general types. The realisation of this fact will make inorganic chemistry, and particularly inorganic qualitative analysis, much easier to the student. Representative reactions to familiarise beginners with the most important types are listed in section 9, 2 (pp. 174–180). The importance of the solubilities of salts in water has been emphasised already (pp. 88–91), and a table of soluble and insoluble salts is given in section 9, 3 (p. 180).

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9, 2   **REPRESENTATIVE REACTIONS**

The following selection illustrates most of the important general types of inorganic reactions, and should give students a " bird's-eye view " of inorganic chemistry.

Reaction of Sodium Hydroxide with the following Salts.

Precipitation of Insoluble Salts—Simple Reactions.

For theory see pp. 85-91. The salts are precipitated by mixing solutions, each containing one of the two ions concerned. Many of the precipitated salts "dissolve" in acids, for the reasons discussed on pp. 111-112.

Complex Ion Formation.

For theory see pp. 87-88.

In all cases except Nos. 66 and 70 a simple precipitation reaction is followed by the "dissolving" of the precipitate in excess reagent, due to the formation of a complex ion.

More Complex Reactions.

SIMPLE IONIC REACTIONS

Neutralisation and Related Reactions. Salt Formation.

For theory see p. 188.

Displacement of one Acid or Base by another.

For theory see pp. 108–109.

Reactions of Hydrochloric Acid with the following Salts

	Type of Complex	Ion		
64.	Cyanide	Ferrocyanide	C, 26	p. 218
65.	Thiocyanate	Ferrithiocyanate	C, 34	p. 220
66.	Molybdate	Phosphomolybdate	P, 7	p. 236
67.	Water	Cupric (hydrated)	O, 8	p. 245
68.	Ammonia	Cuprammonium	Cu, 9b	p. 193
69.	Ammonia	Silver-ammonium	Ag, 6	p. 195
70.	Nitric oxide	Ferrous-nitric oxide	N, 31	p. 233

No. 70 is the " Brown Ring " test for nitrate.

Related Reaction.

71. Precipitation of basic bismuth salt (BiO⁺ ion)   Bi, 1   .   p. 242

DOUBLE DECOMPOSITIONS

Ionic reactions in water, formerly considered as double decompositions, are listed above.

Reactions of Concentrated Sulphuric Acid with Salts.

See pp. 186 and 251.

	Salt	Type of Reaction		
72.	Sodium chloride	Simple displacement	Cl, 4	p. 260
73.	Potassium iodide	Displacement and oxidation	I, 5a	p. 265
74.	Sodium formate	Displacement and dehydration	C, 9	p. 215
75.	Sodium nitrate	Displacement and decomposition	N, 29	p. 233
76.	Sodium phosphate	Simple displacement No visible change.	P, 4	p. 235

Carbonate Fusion.

77.	Calcium phosphate	. . .	C, 17	p. 216

Borax Bead Tests.

See pp. 185 and 209.

78.	Cupric chloride	. . . .	Cu, 5	p. 192
79.	Ferrous sulphate	. . . .	Fe, 5	p. 270

Charcoal Block Tests.

See pp. 185 and 212-213. The first stage in all cases is a double decomposition, which may be followed by decomposition of a metallic carbonate and reduction of the oxide.

80.	Cupric sulphate	Full series of reactions	Cu, 3b	p. 192
81.	Zinc sulphate	Do., followed by partial reoxidation of metal	Zn, 4	p. 202

ADDITION AND REMOVAL OF WATER

Formation of acids or bases from acidic or basic oxides, and the reverse reactions.

Related Reaction.

Formation and Decomposition of Salt Hydrate.

DECOMPOSITION OF SALTS ON HEATING

FLAME TESTS

MISCELLANEOUS

9, 3   SOLUBILITIES OF SALTS

Detailed lists of solubilities are given in the sections of this chapter dealing with the individual anions and cations. The following general statements, in which a number of minor exceptions have been deliberately disregarded, are all that the student needs to remember.

1. All inorganic *acids*, all *sodium*, *potassium* and *ammonium* salts are soluble in water.

2. All *nitrates* and *nitrites* are soluble in water.

3. All *chlorides*, *bromides* and *iodides* are soluble in water *except* those of silver, mercurous and lead,[1] and mercuric iodide. These salts are no more soluble in acids than in water.

4. All *sulphates* are soluble in water *except* those of calcium,[1] strontium, barium and lead. These salts are no more soluble in acids than in water.

5. All *hydroxides, sulphides, sulphites, phosphates* and *carbonates* are insoluble in water but "soluble" in dilute acids *except* the following:

    (a) the sodium, potassium and ammonium compounds, which are soluble in water;

    (b) some sulphides (those of metals in Analytical Groups 1 and 2), which are insoluble in dilute acids;

    (c) bicarbonates, which are soluble in water.

6. Many salts of *arsenic, antimony, bismuth* and *tin* are hydrolysed by water to insoluble basic salts, but dissolve in dilute acids.

9, 4   ARRANGEMENT OF SECTIONS

The information regarding each element and its compounds is arranged on the following plan. In general only the most important compounds and their chief properties are included. The fact that a particular compound is not mentioned here does not necessarily mean that it does not exist, but that it is not sufficiently important to include in an elementary course. However, the behaviour of every anion and cation towards the appropriate general analytical reagents is described, since, as explained in chapter 2 (p. 10), a test is of no

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[1] The halides of lead and calcium sulphate are sparingly soluble.

value unless the behaviour in that test of *every* substance which might be present is known.

Experimental details are given in small type.

THE ELEMENT

Preparation. (A few gaseous non-metals only.)

Physical Properties.[1] State, melting-point, density, colour, smell, solubility in water.

Chemical Properties.[1] Reactions with oxygen, hydrogen, water, if any. Electronegative or electropositive nature. Reactions with other elements.

HYDRIDES

(Of non-metals only.)

Preparation.

Physical Properties. State, colour, smell, solubility in water.

Chemical Properties. Acidic, neutral or basic character. Oxidation-reduction reactions.

Corresponding Anion or Cation. Colour, solubilities of salts. Ionic reactions as for other anions and cations (see below).

ACIDIC OXIDES, OXY-ACIDS AND ANIONS

Acidic Oxide. Preparation, physical properties, formation of acid or acids with water.

Acid.

Physical Properties. State, colour, smell, solubility in water.

Strength. Behaviour of salts with dilute mineral acids.

Stability. Behaviour of salts with concentrated sulphuric acid.

Oxidation-Reduction Reactions.

Salts. Behaviour of solid salts on heating.

Anion.

Colour.

Solubilities of Salts.

Ionic Reactions. These are tabulated. The reactions with hydrogen, silver and barium ions (the general testing reagents for anions) are given in all cases, even if no visible result occurs. Reactions with other cations are given only if important. Subsequent reactions of precipitates with excess reagent or with other substances are noted where necessary in the " Comments " column.

Equations are not given since the reactions all belong to one or other of a few general types. It is a waste of paper to give the equation for a reaction such as that between silver and chloride ions. The student

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[1] Many physical and chemical properties of metals may be deduced if the student remembers the appearance and behaviour of the elements in everyday life (consider, *e g.*, a rusty iron nail, a tin can, an aluminium saucepan).

9, 3   SOLUBILITIES OF SALTS

Detailed lists of solubilities are given in the sections of this chapter dealing with the individual anions and cations. The following general statements, in which a number of minor exceptions have been deliberately disregarded, are all that the student needs to remember.

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   (*a*) the sodium, potassium and ammonium compounds, which are soluble in water ;

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[1] The halides of lead and calcium sulphate are sparingly soluble.

READING

>re each practical class, read the sections of this chapter de-
ıg the elements to be studied.

EXPERIMENTS TO BE DONE AND MATERIALS TO BE USED

vould be undesirable for students to carry out all the reactions
bed in this chapter, even if time permitted, since many reactions
cluded only for reference. Instructors should therefore tell
ıts which reactions they wish them to perform. A representative
on of reactions is listed on pp. 175–180. The preliminary
nation and the tests with water and litmus should be carried out
ıll the substances provided.

: author's practice is to detail on the blackboard the substances to
:d for each test, the total quantity of each substance required, the
ı which each substance is to be obtained (e.g., from a dish on the
ıt's bench, from a stock burette or automatic pipette on the
on bench) and (where necessary) the order in which tests are
done.

STANDARD METHODS

the experiments described here are on the test-tube scale, and
llowing standard quantities and methods should be used unless
instructions are given.

liminary Examination.

te and record the state, colour and smell of each substance
ied.

lubility in Water.

ses. The solubility in water of gases which are *extremely soluble*
ammonia, hydrogen chloride) may be demonstrated as follows :

Open a tube of gas under water. The water immediately rushes
n and fills the tube completely.

e solubilities of gases which are *moderately soluble* (e.g., carbon
de) or *sparingly soluble* (e.g., oxygen) may be examined.

Collect about half a tube of gas by displacement of water.
Level the tube to bring the gas to atmospheric pressure, and mark
the level with a rubber band or loop of cotton. Cork the tube,
shake gas and water together vigorously for a minute, reopen the
tube under water and re-level. If the gas is moderately soluble
an appreciable fraction will have dissolved, and the level will be
higher than it was before. If the gas is sparingly soluble, no
appreciable fraction will have dissolved and the level will be
unchanged.

can deduce for himself from the formula of the product (AgCl) that
this equation is $Ag^+ + Cl^- = AgCl$.

BASIC OXIDES, BASES AND CATIONS

Oxide and Hydroxide.

Physical Properties. Colour, solubility in water.

Basic and Related Properties. Behaviour with dilute acids, caustic alkalis (amphoteric hydroxides) and ammonia (formation of complex ions). Strength of the hydroxide as base.

Reduction of Oxide. Behaviour of oxide (and related compounds) on charcoal block.

Flame Test.

Borax Bead Test.

Cation.

Colour.

Oxidation-Reduction Reactions.

Solubilities of Salts.

Ionic Reactions. These are tabulated. The reactions with the principal precipitating agents (chloride, sulphide, hydroxide and carbonate) are given in all cases, even if there is no visible change. Details are given both for the simple reagents, *e.g.*, sodium hydroxide, and for the modified reagents used in the common Group Separation method, *e.g.*, ammonium hydroxide plus ammonium chloride. Reactions with other anions are given only if important. Subsequent reactions of precipitates with excess of reagent or with other substances are noted if necessary in the " Comments " column. Equations are not given for the reasons stated in the note on anions above.

Analytical Behaviour. The behaviour of the cation in the Group Separation is explained. The cations are classified according to the solubility of their sulphides in three classes, A, B and C, as described on pp. 90–91. (*This nomenclature is the author's own.*) The numbering of the Analytical Groups (1, 2, 3, 4, 5, 6) follows common practice.

OTHER OXIDES

These are mainly neutral oxides of non-metals, and peroxides of metals. Important physical and chemical properties are detailed.

MISCELLANEOUS COMPOUNDS

These are mainly covalent compounds formed by pairs of non-metals (*e.g.*, *phosphorus and chlorine*). Important physical and chemical properties are detailed.

BIOLOGICAL RÔLE AND MEDICAL USES

These are briefly noted as explained on p. 174.

7. Heating of Solids Alone.

Take the solid (1 spatula-point) in a hard-glass ignition-tube. Heat the tube in the Bunsen flame, holding it in an almost horizontal position so that liquids which distil and condense in the cooler parts of the tube do *not* run back on to the hot solid.

8. Charcoal Block Tests.

For theory see under Carbon, pp. 212-213.

In a clean part of the charcoal block scrape a hole about $\frac{1}{8}$ in. deep and $\frac{1}{4}$ in. in diameter. Mix the substance ($\frac{1}{2}$ spatula-point) with anhydrous sodium carbonate ($\frac{1}{2}$ spatula-point), fill the hole with this mixture and heat it with a reducing blowpipe flame. This is produced from the luminous Bunsen flame (air-hole closed) by holding the nozzle of the blowpipe just outside the flame and blowing gently so that the substance is heated by the inner cone of the flame. Note the smell of any vapours evolved and the nature of any bead or incrustation left at the end of the test.

9. Flame Test.

This test is carried out by heating the substance on a platinum wire in the Bunsen flame. The platinum wire is conveniently stored in a test-tube half-full of concentrated hydrochloric acid. Hydrochloric acid is used to clean the wire and to produce the flame colours because only volatile salts of a metal give its characteristic flame colour, and chlorides are usually the most volatile salts. The use of cobalt glass in connection with the flame test for potassium is discussed on p. 190.

The wire must be clean ; it may be considered clean only if after being dipped into a little concentrated hydrochloric acid on a watch-gl . . .   the flame, it r . . .   hydro-chloric aci . . .   the flame. When the wire is clean, mix the substance to be tested ($\frac{1}{4}$ spatula-point) with concentrated hydrochloric acid (2 drops), take a trace of the mixture on the wire and heat the latter in the outer edge of the oxidising flame of the Bunsen burner.

10. Borax Bead Tests.

For theory see p. 209.

Coil the end of the platinum wire into a loop of about 2 mm. diameter. Heat this in the Bunsen flame (oxidising part of the non-luminous flame), dip it into powdered borax and reheat in the same flame. The salt swells up, then shrinks, and forms a glassy bead. Touch this bead against a trace of the solid to be tested and heat, first in the reducing flame, then in the oxidising flame. In each case allow the bead to cool before noting the colour produced.

Liquids. The miscibility of the liquid with water over the whole range from 100% water to 100% liquid is investigated thus:

Solids. The method described above for a liquid gives a roughly quantitative idea of its miscibility with water. A similar method for a solid would involve much weighing; the following method should therefore be used to save time:

> Add the solid (1 spatula-point)[1] to water (2 ml.) in a test-tube and grind up with a glass rod. If the substance does not dissolve completely, heat gently to boiling and allow to cool slowly. Note all that happens.

One " spatula-point " represents anything from 0·05 g. to 0·2 g. solid; solids which do not dissolve completely in these conditions probably have solubilities of less than 10 g. per 100 ml.

3. *Comparison of the Density of a Gas with that of Air.*

If a gas is coloured or can be recognised by some not-over-sensitive test, and if its density differs *greatly* from that of air, this comparison may be carried out as follows:

> Take two corked tubes of the gas. Hold one *mouth downwards*, uncork it for 10 seconds, and re-cork; repeat with the other tube, held *mouth upwards*. Test the contents of the tubes for the gas.

If the gas is denser than air it will escape from the " mouth downwards " tube; if it is less dense than air it will escape from the " mouth upwards " tube.

4. *Behaviour with Litmus.*

Test the aqueous solution or suspension of each substance with litmus-paper. Note and record results and conclusions.

5. *Preparation of Gases.*

Standard apparatus for the preparation and collection of gases is described on pp. 26-27.

6. *Testing for Gases.*

Colourless, odourless gases must be recognised by the production of visible effects with test solutions or papers. If the gas is produced in quantities sufficient to fill a test-tube, the usual gas preparation apparatus may be used (see pp. 26-27).

> For smaller-scale work, carry out the reaction in which the gas is evolved in a boiling-tube (1 in. diameter) and insert the test paper or rod carrying a drop of the test solution *without allowing it to touch the sides of the tube.*

[1] This arbitrary measure for solids is illustrated on p. 443.

Reactions.

The following were carried out ; results were as stated in the book except as detailed below.

1. *Preparation of Chlorine.*
$$MnO_2+4HCl = MnCl_2+2H_2O+Cl_2\uparrow.$$
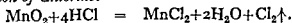
3. *Chlorine as an Oxidising Agent.*
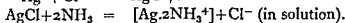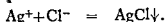Chlorine water and potassium iodide solution $Cl_2+2I^-=I_2+2Cl^-$. At the first attempt, the solution did not go brown. It was suspected that the chlorine water was old ; it was almost odourless. The test was repeated, using a fresh specimen of chlorine water which smelt strongly of chlorine, and was successful.

Etc. etc.

Reactions of the chloride ion (sodium chloride solution used).

10. Dil. HCl—No change.

11. $AgNO_3$ solution—White ppt. of AgCl, insol. in dil. HNO_3, sol. in dil. NH_4OH.
$$Ag^++Cl^- = AgCl\downarrow.$$
$$AgCl+2NH_3 = [Ag.2NH_3^+]+Cl^- \text{ (in solution)}.$$
Etc. etc.
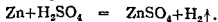
9, 7   **HYDROGEN**

Valency : 1.   *Oxides :* H_2O, H_2O_2.   *Cation :* H^+.

Hydrogen is unique in its chemical nature and cannot properly be considered as part of any Group in the Periodic Table ; it shows resemblances both to the alkali metals and to the halogens.

. . . . 'H_2), insoluble in water. . . . . or oxygen quietly with . . . . of hydrogen with air or oxygen explodes on ignition. Coal-gas contains about 50% by volume of hydrogen.

$$2H_2+O_2 = 2H_2O.$$
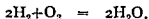
Hydrogen may be made by the action of dilute acids on metals.
$$Zn+H_2SO_4 = ZnSO_4+H_2\uparrow.$$

1. *Preparation of Hydrogen.*
Gas Apparatus Type B. 1. Treat zinc (2 small pieces) with dilute sulphuric acid (20 ml.) to which cupric sulphate solution (2 drops) has been added as . . . .

2. Apply a burning splint to the mouth of a tube of hydrogen ; the gas burns with a blue flame.

11. Reaction between Concentrated Sulphuric Acid and a Solid.

Take the solid (1 spatula-point) in a *dry* test-tube. Add concentrated sulphuric acid dropwise (1 ml.). Shake cautiously and heat cautiously, with shaking, pointing the tube in such a direction that its contents cannot spurt over your neighbour or yourself. *Allow the tube to cool before pouring the contents into water.*

12. Reaction between two Aqueous Solutions.

Take one solution (1 ml.) in a test-tube, and add the second solution dropwise. If a visible change occurs, continue adding the second solution until no further change takes place. If no visible change occurs with the first few drops, add about 1 ml. of the second solution.

13. Reaction between an Aqueous Solution and a Solid.

Take the solid (1 spatula-point) in a *dry* test-tube or boiling-tube and add the solution dropwise (1 ml.). Heat gently to boiling with shaking if instructed.

9, 6   REPORTS

The following form of report includes everything which the student has found out for himself, but does not include details of experiments which merely confirm what the book says. Any results which are *not* as expected must be noted, and an explanation obtained (by the student himself or from a demonstrator). Equations for reactions should be given, since many equations are deliberately omitted in this book.

26 Nov. 1945.

REACTIONS OF CHLORINE AND ITS COMPOUNDS

Reference.—Klyne, *Practical Chemistry*, Section 9, 34, pp. 258-262.

Examination of Substances.

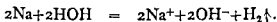| Substances studied	Appearance and smell	Solubility in water	Behaviour with litmus
Chlorine, Cl_2.	Greenish-yellow gas; denser than air. Choking smell.	Moderately soluble.	Bleaches litmus.
Hydrogen chloride, HCl	Colourless gas; denser than air. Acid smell.	Very soluble.	Turns litmus red; therefore acid.
Sodium chloride, NaCl	White crystalline solid. No smell.	Soluble.	Litmus unchanged; therefore neutral.

sodium, potassium, etc.) are highly electropositive, and their hydroxides are strong bases. They show a very strong family resemblance. The B Subgroup metals (the "*currency*" *metals*, copper, silver, etc.) are electronegative elements, and their hydroxides are weak bases. Copper often shows an "abnormal" valency of 2.

9, 8   SODIUM

Valency: 1.   *Oxides*: Na_2O, Na_2O_2.   *Cation*: Na^+.

Sodium is a soft light fusible metal (m.p.=96°, d=0·97). It is very electropositive, and is readily attacked by oxygen (forming the oxide Na_2O) and by water (forming the hydroxide NaOH, with evolution of hydrogen).

$$2Na + 2HOH = 2Na^+ + 2OH^- + H_2\uparrow.$$

The bright surface of a freshly-cut piece of sodium tarnishes very rapidly. The metal is usually kept under an inert hydrocarbon solvent (*e.g.*, toluene), in which neither water nor oxygen is appreciably soluble. Sodium is much used for drying organic liquids with which it does not react.

1. To sodium wire [1] (¼ inch) add water (1 ml.). Note the vigorous evolution of hydrogen, and show that the resulting solution turns litmus blue.

The oxide Na_2O will not be met. The peroxide (Na_2O_2), a white solid, is a powerful oxidising agent. It must not be allowed to touch organic materials (*e.g.*, paper or clothes) since it may set fire to them. It reacts vigorously with water, oxygen being evolved.

$$2Na_2O_2 + 2H_2O = 4Na^+ + 4OH^- + O_2\uparrow.$$

2. To sodium peroxide (¼ spatula-point) add water (1 ml.). Test the evolved gas for oxygen.

The hydroxide (caustic soda, NaOH) is a white deliquescent solid and a strong base. It and its solutions rapidly absorb carbon dioxide from the air forming the carbonate. Its solutions attack most kinds of glass; they must be washed out of measuring instruments (*e.g.*, burettes) as soon as possible after use, and it is advisable to keep them in bottles with rubber stoppers (*not* glass stoppers).

The properties of some important sodium salts are considered in the sections dealing with their anions. Since sodium oxide is not reduced by charcoal, and since most sodium salts (unlike the corresponding salts of other metals) are stable to heat, sodium compounds give no characteristic reaction on the charcoal block.

All sodium compounds—either in the solid state or in solution—

[1] Take this from the stock bottle and dry rapidly with filter-paper.

Hydrogen is a reducing agent ; it reduces many metallic oxides to metals. $CuO + H_2 = Cu + H_2O$ (not convenient for students' experiment). It combines with many non-metals (*e.g.*, halogens). These reactions are not convenient for use here. " Nascent " hydrogen is a more powerful reducing agent than gaseous hydrogen, and reduces many substances which the latter does not (*e.g.*, ferric salts).

3. (*a*) Bubble hydrogen from the gas-apparatus through ferric chloride solution. No reduction takes place.

(*b*) To ferric chloride solution (2 ml.) and dilute hydrochloric acid (2 ml.) add a small piece of granulated zinc. Nascent hydrogen reduces the ferric salt to ferrous (colour changes from yellow to pale green).

HYDROGEN ION

The hydrogen ion H^+ is the cation common to all acids. Hydrogen ions are present in all aqueous solutions since water dissociates slightly. $HOH \rightleftharpoons H^+ + OH^-$. The problems of hydrogen-ion concentration in aqueous solutions are discussed at length on pp. 91–112.

The neutralisation of an acid by a base to form a salt consists essentially in the combination of hydrogen and hydroxyl ion to form water (see reaction 5). The hydrogen ion is colourless. All common inorganic acids are soluble in water except silicic acid (insoluble) and boric acid (slightly soluble).[1] Precipitation reactions are not used for the detection of the hydrogen ion.

The ion is recognised by the effect of its solutions on acid-base indicators (for full discussion see pp. 98–100) and by its power of liberating carbon dioxide from carbonates.

$$CO_3^{--} + 2H^+ = H_2CO_3 = CO_2 + H_2O.$$

4. Show that dilute hydrochloric acid turns litmus-paper red.

5. *Salt Formation.*

Take in a porcelain basin dilute sodium hydroxide (approximately 2M, 5 ml.)
and add dilute   pipette
                                                                         on the

6. Treat dilute hydrochloric acid with sodium carbonate solution and note the effervescence.

Analytical Behaviour.

Since all common acids are soluble in water, the hydrogen ion is in Class C, Group 6, of the Cation Separation.

PERIODIC GROUP I

The elements of this group are all metals which form cations and show the group valency of 1. They belong, however, to two very different types. The " typical " and A Subgroup elements (the *alkali metals,*

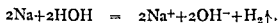[1] Many organic acids are insoluble in water.

sodium, potassium, etc.) are highly electropositive, and their hydroxides are strong bases. They show a very strong family resemblance. The B Subgroup metals (the "*currency*" metals, copper, silver, etc.) are electronegative elements, and their hydroxides are weak bases. Copper often shows an "abnormal" valency of 2.

9, 8   SODIUM

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Sodium is a soft light fusible metal (m.p.$=96°$, $d=0.97$). It is very electropositive, and is readily attacked by oxygen (forming the oxide Na_2O) and by water (forming the hydroxide NaOH, with evolution of hydrogen).

$$2Na + 2HOH = 2Na^+ + 2OH^- + H_2\uparrow.$$

The bright surface of a freshly-cut piece of sodium tarnishes very rapidly. The metal is usually kept under an inert hydrocarbon solvent (*e.g.*, toluene), in which neither water nor oxygen is appreciably soluble. Sodium is much used for drying organic liquids with which it does not react.

1. To sodium wire [1] ($\frac{1}{4}$ inch) add water (1 ml.). Note the vigorous evolution of hydrogen, and show that the resulting solution turns litmus blue.

The oxide Na_2O will not be met. The peroxide (Na_2O_2), a white solid, is a powerful oxidising agent. It must not be allowed to touch organic materials (*e.g.*, paper or clothes) since it may set fire to them. It reacts vigorously with water, oxygen being evolved.

$$2Na_2O_2 + 2H_2O = 4Na^+ + 4OH^- + O_2\uparrow.$$
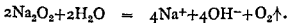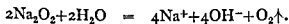
2. To sodium peroxide ($\frac{1}{4}$ spatula-point) add water (1 ml.). Test the evolved gas for oxygen.

The hydroxide (caustic soda, NaOH) is a white deliquescent solid and a strong base. It and its solutions rapidly absorb carbon dioxide from the air forming the carbonate. Its solutions attack most kinds of glass; they must be washed out of measuring instruments (*e.g.*, burettes) as soon as possible after use, and it is advisable to keep them in bottles with rubber stoppers (*not* glass stoppers).

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[1] Take this from the stock bottle and dry rapidly with filter-paper.

Hydrogen is a reducing agent; it reduces many metallic oxides to metals. $CuO + H_2 = Cu + H_2O$ (not convenient for students' experiment). It combines with many non-metals (e.g., halogens). These reactions are not convenient for use here. " Nascent " hydrogen is a more powerful reducing agent than gaseous hydrogen, and reduces many substances which the latter does not (e.g., ferric salts).

3. (a) Bubble hydrogen from the gas-apparatus through ferric chloride solution. No reduction takes place.
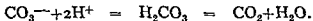
(b) To ferric chloride solution (2 ml.) and dilute hydrochloric acid (2 ml.) add a small piece of granulated zinc. Nascent hydrogen reduces the ferric salt to ferrous (colour changes from yellow to pale green).

HYDROGEN ION

The hydrogen ion H^+ is the cation common to all acids. Hydrogen ions are present in all aqueous solutions since water dissociates slightly. $HOH \rightleftharpoons H^+ + OH^-$. The problems of hydrogen-ion concentration in aqueous solutions are discussed at length on pp. 91–112.

The neutralisation of an acid by a base to form a salt consists essentially in the combination of hydrogen and hydroxyl ions to form water (see reaction 5). The hydrogen ion is colourless. All common inorganic acids are soluble in water except silicic acid (insoluble) and boric acid (slightly soluble).[1] Precipitation reactions are not used for the detection of the hydrogen ion.

The ion is recognised by the effect of its solutions on acid-base indicators (for full discussion see pp. 98–100) and by its power of liberating carbon dioxide from carbonates.

$$CO_3^{--} + 2H^+ = H_2CO_3 = CO_2 + H_2O.$$

4. Show that dilute hydrochloric acid turns litmus-paper red.

5. Salt Formation.

Take in a porcelain basin dilute sodium hydroxide (approximately 2M, 5 ml.) and add dilute hydrochloric acid (approximately 2M) from a graduated pipette until the mixture is neutral to litmus-paper. Evaporate to dryness on the boiling water bath. Sodium chloride remains as a white solid.

6. Treat dilute hydrochloric acid with sodium carbonate solution and note the effervescence.

Analytical Behaviour.

Since all common acids are soluble in water, the hydrogen ion is in Class C, Group 6, of the Cation Separation.

PERIODIC GROUP I

The elements of this group are all metals which form cations and show the group valency of 1. They belong, however, to two very different types. The " typical " and A Subgroup elements (the alkali metals,

[1] Many organic acids are insoluble in water.

1. *Flame Test.* Observe with the naked eye and through cobalt glass the flame colours produced by

(a) Potassium chloride (1M solution) free from sodium.
(b) Potassium chloride (1M solution) containing sodium chloride (0·01M).
(c) Sodium chloride (1M solution) free from potassium.

The potassium ion K+ is colourless.

All the common potassium salts are soluble in water, but the potassium salts of some rarer acids (*e.g.*, the cobaltinitrite, perchlorate, and acid tartrate) are sparingly soluble, while the corresponding sodium salts are readily soluble. The precipitation of these salts can therefore be used to distinguish potassium from sodium. (All other cations, including ammonium, must be absent.)

IONIC REACTIONS

Use potassium chloride (0·2M solution)

No.	Reagent	Visible Results	Comments
2	Cobaltinitrite Na$_3$[Co(NO$_2$)$_6$].	Yellow ppt., K$_3$[Co(NO$_2$)$_6$].	
3	Acid tartrate Na.HC$_4$H$_4$O$_6$.	White ppt., K.HC$_4$H$_4$O$_6$.	Ppt. in conc. solns. only.
4	Perchlorate HClO$_4$.	White ppt., KClO$_4$.	Ppt. in conc. solns. only.

Analytical Behaviour.

Since all common potassium salts are soluble in water, potassium is in Class C, Group 6 of the Cation Separation.

BIOLOGICAL RÔLE

Potassium plays a most important rôle in connection with excitability of tissues, especially of nerve and muscle. In man it is mainly intracellular ; the concentration in plasma is low but shows considerable variations. The potassium ion passes through cell membranes more readily than all other cations.

9, 10   **COPPER**

Valencies : 1, 2.   *Oxides* : Cu$_2$O, CuO.   *Cations* : Cu+, Cu++.

Copper is a heavy red metal (m.p. 1083° ; d = 8·95), which is not readily oxidised by air. Copper is below hydrogen in the electrochemical

give an *intense yellow* colour to the Bunsen flame. This test is very sensitive.

3. *Charcoal Block Test.* Use sodium sulphate.
4. *Flame Test.* Use sodium carbonate solution.

The sodium ion Na+ is colourless. The sodium salts of all common and most less common acids are soluble in water. An exception is the antimonate (NaH_2SbO_4), which is precipitated by potassium antimonate (KH_2SbO_4).

IONIC REACTION
Use sodium chloride (0·2M solution)

No.	Reagent	Visible Result	Comments
5	Antimonate KH_2SbO_4.	White ppt. NaH_2SbO_4.	NH_4 and all metals other than Na or K must be absent. Solution must not be acid.

Analytical Behaviour.

Since all common sodium salts are soluble in water, sodium is in Class C, Group 6 of the Cation Separation.

BIOLOGICAL RÔLE

Sodium is quantitatively the most important inorganic cation in living organisms. In man it occurs chiefly in extracellular fluids. (Plasma normally contains about 300-350 mg. per 100 ml., but large variations in concentration are possible without serious physiological effects).

9, 9   **POTASSIUM**

   Valency: 1.   *Oxide:* K_2O.   *Cation:* K+.

Potassium and its compounds resemble sodium and its compounds closely in nearly all respects. The metal is strongly *electropositive*, and the hydroxide (caustic potash, KOH) is a strong base.

All potassium compounds—either in the solid state or in solution—give to the Bunsen flame a *lilac* colour, which is very often " masked " by the *yellow* colour produced by traces of sodium compounds present as impurities. The potassium flame can, however, be distinguished if the flame is observed through cobalt glass. Cobalt glass does not transmit the orange light produced by sodium compounds in the flame; the flame produced by a pure sodium compound is therefore almost invisible through cobalt glass. The flame of a potassium compound (whether contaminated with sodium or not) appears a beautiful reddish-violet colour when seen through cobalt glass.

1. *Flame Test.* Observe with the naked eye and through cobalt glass the flame colours produced by

(a) Potassium chloride (1M solution) free from sodium.
(b) Potassium chloride (1M solution) containing sodium chloride (0·01M).
(c) Sodium chloride (1M solution) free from potassium.

The potassium ion K+ is colourless.

All the common potassium salts are soluble in water, but the potassium salts of some rarer acids (*e.g.*, the cobaltinitrite, perchlorate, and acid tartrate) are sparingly soluble, while the corresponding sodium salts are readily soluble. The precipitation of these salts can therefore be used to distinguish potassium from sodium. (All other cations, including ammonium, must be absent.)

IONIC REACTIONS

Use potassium chloride (0·2M solution)

No.	Reagent	Visible Results	Comments
2	Cobaltinitrite $Na_3[Co(NO_2)_6]$.	Yellow ppt., $K_3[Co(NO_2)_6]$.	
3	Acid tartrate $Na.HC_4H_4O_6$.	White ppt., $K.HC_4H_4O_6$.	Ppt. in conc. solns. only.
4	Perchlorate $HClO_4$.	White ppt., $KClO_4$.	Ppt. in conc. solns. only.

Analytical Behaviour.

Since all common potassium salts are soluble in water, potassium is in Class C, Group 6 of the Cation Separation.

BIOLOGICAL RÔLE

Potassium plays a most important rôle in connection with excitability of tissues, especially of nerve and muscle. In man it is mainly intracellular; the concentration in plasma is low but shows considerable variations. The potassium ion passes through cell membranes more readily than all other cations.

9, 10   COPPER

Valencies : 1, 2.   *Oxides :* Cu_2O, CuO.   *Cations :* Cu^+, Cu^{++}.

Copper is a heavy red metal (m.p. 1083°; $d = 8·95$), which is not readily oxidised by air. Copper is below hydrogen in the electrochemical

series. It therefore does not react with water, and does not dissolve in acids except those which are also oxidising agents, viz. concentrated sulphuric acid, which is reduced to sulphur dioxide (see p. 251), and nitric acid, which is reduced to a variety of products (see pp. 230-232).

1. Examine the behaviour of copper (a few small turnings) with (a) dilute hydrochloric acid, and (b) concentrated nitric acid.

Copper forms two series of compounds, *cuprous* (in which it is univalent) and *cupric* (in which it is divalent). Cuprous compounds will be met here only as the reduction products of cupric compounds. Most simple cuprous compounds are insoluble in water. Many are white, but the oxide (Cu_2O) is red.

Cupric oxide (CuO, black) and hydroxide ($Cu(OH)_2$, pale blue) are insoluble in water, but "soluble" in dilute acids. Cupric hydroxide "dissolves" in dilute ammonium hydroxide, since the hydroxide of the complex ion $[Cu.4NH_3]^{++}$ is soluble in water. Cupric hydroxide is a *weak* base. Cupric oxide may be reduced to metallic copper by heating in a stream of hydrogen (not suitable for students' experiment), or by heating with charcoal.

2. Show that cupric oxide is insoluble in water but "soluble" in dilute hydrochloric acid.

3. *Charcoal Block*. Reduce (a) cupric oxide, and (b) cupric sulphate to copper (red grains).

Volatile copper compounds colour the Bunsen flame bluish-green. When heated in the borax bead copper compounds give a green bead (cupric borate) in the oxidising flame and a red bead in the reducing flame.

4, 5. Use cupric chloride for the flame test and borax bead test.

The cupric ion, which is really $[Cu.4H_2O]^{++}$, is blue, and many solid cupric compounds are blue or green. The complex ion $[Cu.4NH_3]^{++}$ is a *much* deeper blue than $[Cu.4H_2O]^{++}$.

Cupric compounds in solution may be reduced to cuprous compounds by iodide ions (see reaction 6 below), arsenite (see p. 238), and many organic compounds, including simple aldehydes (pp. 333-334) and some carbohydrates (pp. 388-390).

$$Cu^{++} + e = Cu^+$$

or

$$2CuO = Cu_2O + (O).$$
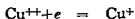
6. *Potassium iodide* solution reduces cupric to cuprous salts, the iodide being itself oxidised to iodine (brown solution); CuI (white) is insoluble in water, and is therefore precipitated at the same time.

$$2Cu^{++} + 4I^- = 2CuI + I_2$$

CUPRIC SALTS

Solubilities of Salts.

Chloride, bromide, sulphate, nitrate .	Soluble in water.
Carbonate, phosphate . . .	Insoluble in water, " soluble " in dilute hydrochloric acid.
Sulphide	Insoluble in water and in dilute acids.
Iodide	Does not exist.

IONIC REACTIONS

Use cupric sulphate (0·2M solution)

No.	Reagent	Visible Result	Comments
7	**Chloride** Dil. HCl . .	None.	$CuCl_2$ is sol.
8	**Sulphide** (a) H_2S+dil. HCl . (b) H_2S+NH_4Cl+ NH_4OH.	Black ppt., CuS. ,, ,,	
9	**Hydroxide** (a) NaOH . (b) NH_4OH .	Pale blue ppt., $Cu(OH)_2$. Pale blue ppt., first; then deep blue * soln. containing $[Cu_4NH_3]^{++}$.	On heating gives black CuO. $[Cu_4NH_3](OH)_2$ is soluble.
10	**Carbonate** (a) Na_2CO_3 . (b) $(NH_4)_2CO_3$.	Pale blue ppt., $CuCO_3$ (basic). Pale blue ppt., first; then deep blue soln.	$[Cu_4NH_3]CO_3$ is soluble.
11	**Ferrocyanide** $K_4[Fe(CN)_6]$.	Brown gelatinous ppt., $Cu_2[Fe(CN)_6]$.	Used as semi-permeable membrane for osmosis.

* The formation of the cuprammonium ion is used as a test for copper at concentrations at which the colour of the hydrated ion is invisible.

Analytical Behaviour.

Cupric sulphide is insoluble in water and dilute acids, while the chloride is soluble in water ; the cupric ion is therefore in Class A, Group 2 in the Cation Separation.

BIOLOGICAL RÔLE AND MEDICAL USES

Copper (in very small quantities) is essential for mammalian life ; it plays a part in the formation of red blood cells.

Cupric salts are astringents, and cupric sulphate is used in medicine externally as a caustic and internally as an emetic. Copper compounds are poisonous if taken into the system in large quantities.

9, 11   **SILVER**

Valency : 1.   *Oxide :* Ag_2O.   *Cation :* Ag^+.

Silver is a heavy metal (m.p.=961° ; d=10·5), which is not oxidised by air or oxygen. It is below hydrogen in the electrochemical series, *and is therefore not affected by water, dilute hydrochloric acid or dilute sulphuric acid.* It is, however, "dissolved" by the oxidising acids, dilute and concentrated nitric acid and concentrated sulphuric acid.

The brown oxide Ag_2O is decomposed on heating, giving the metal and oxygen, $2Ag_2O=4Ag+O_2$; compare mércuric oxide. The hydroxide AgOH is unknown. Silver compounds when heated with sodium carbonate and charcoal yield metallic silver.

1. Treat silver (one small turning) with concentrated nitric acid.
2. Heat silver oxide (½ spatula-point)
3. *Charcoal Block Test.* Use silver nitrate.

The simple silver ion and all complex silver ions which will be met here are colourless.

Solubilities of Salts.

The majority of silver salts are insoluble in water, and as a number of these are variously coloured, the Ag^+ ion (silver nitrate solution) is an ideal general testing reagent for anions. The only common inorganic silver salts which are soluble in water are the nitrate, sulphate (sparingly) and nitrite (sparingly). Many of the salts insoluble in water are "soluble" *either* in dilute nitric acid (salts of weak acids, *e.g.*, phosphate, see pp. 111-112), *or* in ammonium hydroxide (due to the formation of the complex cation $[Ag.2NH_3]^+$, many of whose salts are soluble), *or* in a solution of the alkali salt of the anion concerned (due to the formation of a complex anion, *e.g.*, cyanide $[Ag(CN)_2]^-$).

IONIC REACTIONS

Use silver nitrate (0·1M solution)

No.	Reagent	Visible Result	Comments
4	**Chloride** Dil. HCl .	White ppt., AgCl.	Insol. in dil. HNO₃. Sol. in dil. NH₄OH, giving [Ag.2NH₃]Cl.
5	**Sulphide** (a) H₂S+dil. HCl (b) H₂S+NH₄Cl +NH₄OH.	Black ppt. Ag₂S. „ „	
6	**Hydroxide** (a) NaOH . (b) NH₄OH .	Dark brown ppt. Ag₂O. „ „	Insol. in excess NaOH. Sol. in excess NH₄OH, giving [Ag 2NH₃]OH.
7	**Carbonate** (a) Na₂CO₃ . (b) (NH₄)₂CO₃	White ppt. Ag₂CO₃. „ „	Sol. in dil. HNO₃. Sol. in excess NH₄OH, giving [Ag.2NH₃]₂CO₃.
8	**Iodide** KI . .	Yellow ppt. AgI.	Insol. in dil. HNO₃ or dil. NH₄OH.
9	**Chromate** K₂CrO₄ .	Reddish-brown ppt. Ag₂CrO₄.	Sol. in dil. HNO₃.

Analytical Behaviour.

Silver sulphide is insoluble in water and dilute acid; silver is therefore a cation of Class A. Since its chloride is insoluble, it is precipitated by hydrochloric acid in Group 1 of the Cation Separation.

MEDICAL USES

Silver salts are astringents and antiseptics. Silver nitrate is used as a caustic; silver proteinates are used as disinfectants. Silver metal is used for sutures and clips in surgery, since it is inert and does not react with oxidising enzymes.

IONIC REACTIONS

Use silver nitrate (0·1M solution)

No.	Reagent	Visible Result	Comments
4	**Chloride** Dil. HCl .	White ppt., $AgCl$.	Insol. in dil. HNO_3. Sol. in dil. NH_4OH, giving $[Ag.2NH_3]Cl$.
5	**Sulphide** (a) H_2S+dil. HCl (b) H_2S+NH_4Cl +NH_4OH.	Black ppt. Ag_2S. „ „	
6	**Hydroxide** (a) $NaOH$. (b) NH_4OH .	Dark brown ppt. Ag_2O. „ „	Insol. in excess $NaOH$. Sol. in excess NH_4OH, giving $[Ag\,2NH_3]OH$.
7	**Carbonate** (a) Na_2CO_3 . (b) $(NH_4)_2CO_3$	White ppt. Ag_2CO_3. „ „	Sol. in dil. HNO_3. Sol. in excess NH_4OH, giving $[Ag.2NH_3]_2CO_3$.
8	**Iodide** KI . .	Yellow ppt. AgI.	Insol. in dil. HNO_3 or dil. NH_4OH.
9	**Chromate** K_2CrO_4 .	Reddish-brown ppt. Ag_2CrO_4.	Sol. in dil. HNO_3.

Analytical Behaviour.

Silver sulphide is insoluble in water and dilute acid; silver is therefore a cation of Class A. Since its chloride is insoluble, it is precipitated by hydrochloric acid in Group 1 of the Cation Separation.

MEDICAL USES

Silver salts are astringents and antiseptics. Silver nitrate is used as a caustic; silver proteinates are used as disinfectants. Silver metal is used for sutures and clips in surgery, since it is inert and does not react with oxidising enzymes.

PERIODIC GROUP II

The elements of this group are all metals and form cations, but belong to two rather different types. All show the group valency of 2. The " typical " and A Subgroup elements (magnesium, calcium, strontium and barium) are highly electropositive, and form strongly basic hydroxides. Calcium, strontium, and barium (the *alkaline earth metals*) show a very strong family resemblance. The B Subgroup elements (zinc, cadmium and mercury) are a heterogeneous collection ; the chemistry of mercury shows many unique features. For details see the individual sections.

9, 12   MAGNESIUM

Valency : 2.   *Oxide* : MgO.   *Cation* : Mg^{++}.

Magnesium is a light white metal (m.p.=650°; d=1·74) which oxidises very slowly in air at room temperature, but burns with a dazzling white flame if heated in air, giving the oxide. $2Mg+O_2=2MgO$.

Magnesium is electropositive (not as strongly as the alkali and alkaline earth metals). It does not react with cold water, but " dissolves " readily in all dilute acids. $Mg+2H^+=Mg^{++}+H_2\uparrow$. Magnesium does *not* dissolve in caustic alkalis (contrast some similar metals, *e.g.*, zinc).

The oxide (MgO, white solid) reacts with water to give the basic hydroxide (Mg(OH)$_2$, white solid) which, although only sparingly soluble in water, forms sufficient hydroxyl ions to turn red litmus blue. The oxide and hydroxide " dissolve " in all dilute mineral acids.

Magnesium oxide is not reduced by carbon. Magnesium compounds when heated on the charcoal block yield therefore a white residue of the oxide (incandescent when hot).

1. Burn magnesium ribbon (1 inch) holding it in a pair of forceps. Use the product for reaction 3.

2. Treat magnesium ribbon (1 inch) with dilute hydrochloric acid.

3. Moisten the oxide prepared in reaction 1 with a drop of water and test this with litmus-paper.

4. Use magnesium sulphate for the charcoal block test.

The ion Mg^{++} is colourless.

Solubilities of Salts.

Halides, sulphate, nitrate .	Soluble in water.
Sulphide. . . .	Hydrolysed by water to the hydroxide and hydrogen sulphide.
Carbonate, phosphate .	Insoluble in water, " soluble " in dilute mineral acids.

IONIC REACTIONS

Use magnesium sulphate (0·2M solution)

No.	Reagent	Visible Result	Comments
5	**Chloride** Dil. HCl	None.	$MgCl_2$ is sol.
6	**Sulphide** (a) H_2S+dil. HCl (b) H_2S+NH_4Cl +NH_4OH.	None.	MgS is hydrolysed to $Mg(SH)_2$.
7	**Hydroxide** (a) NaOH (b) NH_4OH	White ppt., $Mg(OH)_2$. „ „	Insol. in excess NH_4OH but sol. in NH_4Cl, which decreases [OH]⁻ of soln.
8	**Carbonate** (a) Na_2CO_3 (b) $(NH_4)_2CO_3$ (c) NH_4Cl, NH_4OH +$(NH_4)_2CO_3$.	White ppt., $MgCO_3$ (basic). „ „ None.	NH_4Cl decreases $[CO_3]$⁼ of soln. $MgCO_3$ is therefore *not* pptd.
9	**Phosphate** Na_2HPO_4+NH_4Cl +NH_4OH.	White ppt., $MgNH_4PO_4$.	Formation of ppt. is assisted by scratching walls of tube with glass rod.

Analytical Behaviour.

Magnesium sulphide is hydrolysed by water to the soluble hydrosulphide. Magnesium is therefore in Class C in the Cation Separation. Since the carbonate is soluble in the presence of ammonium salts, magnesium is in Group 6.

BIOLOGICAL RÔLE AND MEDICAL USES

Magnesium is essential for human life. It plays an important part in muscle metabolism and is a depressant of the central nervous system. Chlorophyll, the photosynthetic pigment of green plants, is an organic magnesium compound.

Magnesium oxide, carbonate and trisilicate are used as antacids. Magnesium sulphate and other compounds, which form magnesium ions when acted upon by acid in the stomach (e g., the oxide and carbonate), act as purgatives.

CALCIUM

Valency : 2.   *Oxide : CaO.*   *Cation : Ca++.*

Calcium is a light soft metal (m.p.=810° ; d=1·5), which reacts slowly with air in the cold, and burns when heated, giving the oxide : $2Ca+O_2=2CaO$. It is strongly electropositive and reacts with cold water, hydrogen being liberated. $Ca+2HOH=Ca^{++}+2OH^-+H_2\uparrow$.

The oxide (CaO, quicklime) is a white solid, which is incandescent when heated. It reacts vigorously with water to give the hydroxide $(Ca(OH)_2,$ slaked lime). $CaO+H_2O=Ca(OH)_2$. The hydroxide, which is slightly soluble in water, is a strong base, the aqueous solution of which is called " lime water."

Slaked lime and lime water rapidly absorb carbon dioxide from the air, giving calcium carbonate : $Ca(OH)_2+CO_2=CaCO_3+H_2O$. The

itself, and is often used in place of the latter as an absorbent for carbon dioxide and in organic reactions (see, *e.g.*, p. 340).

Calcium oxide is not reduced by charcoal. Calcium compounds when heated on the charcoal block therefore yield white calcium oxide (incandescent when hot).

Calcium salts which are volatile in the Bunsen flame give to it an *orange-red* colour. The chloride is the most volatile salt of calcium ; substances to which the flame test is to be applied should therefore be treated with hydrochloric acid.

1. Burn a few turnings of calcium in a deflagrating-spoon. Keep the residue for reaction 3.

2. Treat calcium turnings (1 spatula-point) with water (1 ml.).

3. Place the product of reaction 1 on a watch-glass and add water (1 drop). Note the production of heat and evolution of steam. Test the product with litmus-paper.

4, 5. *Use calcium carbonate for charcoal block and flame tests.*

Anhydrous calcium chloride has a great affinity for water ; it is used for drying many gases (except ammonia, with which it combines) and organic solvents (except alcohols and amines), and in desiccators.

The calcium ion Ca++ is colourless.

Solubilities of Salts.

Halides, nitrate . .	Soluble in water.
Sulphide . . .	Hydrolysed to the hydrosulphide, which is soluble in water.
Sulphate . . .	Sparingly soluble in water, not more soluble in dilute acids.
Carbonate, phosphate .	Insoluble in water, " soluble " in dilute hydrochloric or nitric acids.

IONIC REACTIONS

Use calcium chloride (0·2M solution)

No.	Reagent	Visible Result	Comments
6	Chloride Dil. HCl . .	None.	$CaCl_2$ is sol.
7	Sulphide (a) H_2S+dil. HCl (b) H_2S+NH_4Cl +NH_4OH.	} None.	CaS is hydrolysed to sol. $Ca(SH)_2$.
8	Hydroxide (a) NaOH . (b) NH_4OH . .	White ppt. $Ca(OH)_2$. None.	$Ca(OH)_2$ is rather soluble and is only pptd. when high concs. of Ca^{++} and OH^- are mixed.
9	Carbonate (a) Na_2CO_3. (b) $(NH_4)_2CO_3$. (c) NH_4Cl, NH_4OH +$(NH_4)_2CO_3$	} White ppt. $CaCO_3$.	
10	Sulphate Dil. H_2SO_4 . .	White ppt. $CaSO_4$.	With conc. solns. only; $CaSO_4$ is rather soluble.
11	Phosphate Na_2HPO_4+NH_4Cl +NH_4OH.	White ppt., $Ca_3(PO_4)_2$.	Sol. in dil. HCl.
12	Oxalate $(NH_4)_2C_2O_4$ . .	White ppt. CaC_2O_4.	Sol. in dil. HCl. Insol. in dil. acetic acid.
13	Chromate K_2CrO_4 . .	None.	$CaCrO_4$ is sol.

Analytical Behaviour.

Since calcium forms a soluble hydrosulphide (see above) it is in Class C in the Cation Separation. Since its carbonate is insoluble in water (even in the presence of ammonium ions) it is in Group 5.

BIOLOGICAL RÔLE AND MEDICAL USES

Calcium plays an important part in connection with the excitability of tissues, its effect being antagonistic to that of potassium (it is a depressant of the central nervous system). Small alterations in the calcium concentration of plasma (which is usually about 10 mg. per

100 ml. in man) cause considerable effects. Calcium is concerned with many enzyme systems, *e.g.*, in the clotting of blood and of milk (see pp. 419-421). Calcium phosphate forms the hard matter of bones and teeth.

Calcium is administered in cases of deficiency as hydroxide, phosphate, lactate or gluconate. Calcium carbonate and phosphate are also used as antacids. Calcium sulphate exists as two different hydrates, gypsum $CaSO_4.2H_2O$ and Plaster of Paris $CaSO_4.\frac{1}{2}H_2O$. When the latter substance is made into a paste with water and allowed to stand, it forms a mass of interlocking crystals of gypsum. Since expansion takes place during this process, plaster casts may be made by allowing the paste to set in moulds. Plasters are much used in surgery for the immobilisation of damaged parts.

9, 14   STRONTIUM

Strontium (Sr) is a rare element, intermediate in its properties between calcium and barium. It is included here only out of deference to custom. It is precipitated with calcium and barium in Group 5 in analysis as the carbonate. The following properties are sufficient to distinguish it from these elements.

1. *Flame Test.* Crimson.
2. *Chromate Precipitation.* The chromate $SrCrO_4$ is sparingly soluble in water and " soluble " in dilute acetic acid ; *compare* calcium, *contrast* barium.
3. *Sulphate Precipitation.* The sulphate $SrSO_4$ is intermediate in its solubility in water between those of calcium and barium. Solutions containing strontium ions give a precipitate with saturated calcium sulphate [1] solution ; *compare* barium, *contrast* calcium.

9, 15   BARIUM

Valency : 2.   *Oxides* : BaO, BaO_2.   *Cation* : Ba^{++}.

The chemistry of barium and its compounds is generally similar to that of calcium and its compounds. Barium hydroxide (baryta) is more soluble in water than is calcium hydroxide. It is a strong base, solutions of which are used in volumetric analysis. The white peroxide BaO_2 decomposes on strong heating, giving barium oxide and oxygen. It reacts with cold dilute mineral acids to give a solution containing hydrogen peroxide. On warming with dilute hydrochloric acid, chlorine is evolved.

$$BaO_2 + 2H^+ + 2Cl^- \rightleftharpoons H_2O_2 + Ba^{++} + 2Cl^-.$$
$$H_2O_2 + 2Cl^- \rightleftharpoons Cl_2\uparrow + 2OH^-.$$

Volatile barium salts colour the Bunsen flame *yellow-green* (contrast calcium). Note that volatile copper salts colour the flame bluish-green.

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[1] The precipitate forms slowly in the cold, rapidly on boiling.

1. Heat barium peroxide alone.
2. Examine the behaviour of barium peroxide with dilute hydrochloric acid in the cold and on warming.
3. *Flame Test.* Use barium nitrate.

The barium ion is colourless.

Solubilities of Salts.

These resemble the solubilities of the corresponding calcium salts with the . . . . ;

in v . . . .

in water (" soluble " in dilute mineral acids), while calcium chromate is soluble in water.

IONIC REACTIONS

Use barium nitrate (0·2M solution)

No.	Reagent	Visible Result	Comments
4	**Chloride** Dil. HCl	None.	$BaCl_2$ is sol.
5	**Sulphide** (a) H_2S+dil HCl. (b) H_2S+NH_4Cl +NH_4OH.	} None.	BaS is hydrolysed to sol. $Ba(SH)_2$.
6	**Hydroxide** (a) NaOH (b) NH_4OH.	White ppt. $Ba(OH)_2$. None.	$Ba(OH)_2$ is rather sol. and is pptd. only when high concs. of Ba^{++} and OH^- are mixed.
7	**Carbonate** (a) Na_2CO_3. (b) $(NH_4)_2CO_3$. (c) NH_4Cl, NH_4OH. +$(NH_4)_2CO_3$.	} White ppt. $BaCO_3$.	
8	**Sulphate** Dil. H_2SO_4.	White ppt. $BaSO_4$.	$BaSO_4$ is insoluble and pptd. even from dil. solns.; contrast $CaSO_4$
9	**Phosphate** Na_2HPO_4+NH_4Cl +NH_4OH.	White ppt. $Ba_3(PO_4)_2$.	Sol. in dil. HCl.
10	**Oxalate** $(NH_4)_2C_2O_4$.	White ppt. BaC_2O_4.	Sol. in dil. HCl and in hot dil. acetic acid.
11	**Chromate** K_2CrO_4.	Pale yellow ppt. $BaCrO_4$.	Sol. in dil. HCl. Insol. in dil. acetic acid.

Analytical Behaviour.

Barium, like calcium, falls in Class C, Group 5, of the Cation Separation.

MEDICAL USES

Barium, having a high atomic weight, is opaque to X-rays and is used to render the alimentary canal visible. For this purpose the insoluble *sulphate* is used, since soluble barium salts are very toxic.

9, 16	ZINC

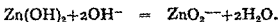|	
Valency : 2.	*Cation* : Zn^{++}.
Oxide : ZnO.	*Anion* : ZnO_2^{--}.

Zinc is a fusible metal of medium density (m.p.$=420°$; $d=6·9$), which is stable in dry air, but in moist air forms a white basic carbonate. If heated in air it burns with a bluish-white flame forming the oxide.
$$2Zn+O_2=2ZnO.$$

The metal does not react with cold water, but " dissolves " readily in dilute acids, giving salts and hydrogen.

$$Zn+2H^+ = Zn^{++}+H_2\uparrow.$$

The metal also " dissolves " in hot caustic alkalis, giving zincates (see below). $Zn+2OH^-=ZnO_2^{--}+H_2\uparrow$.

The oxide (ZnO, white when cold, yellow when hot) and the hydroxide ($Zn(OH)_2$, white) are insoluble in water. The hydroxide is *amphoteric*. When treated with strong acids, it acts as a weak base, " dissolving " to give soluble salts in which Zn^{++} is the cation. $Zn(OH)_2+2H^+=Zn^{++}+2H_2O$. When treated with strong bases, it acts as a weak acid, " dissolving " to give soluble salts in which zinc is part of the anion (zincate ion, ZnO_2^{--}).

$$Zn(OH)_2+2OH^- = ZnO_2^{--}+2H_2O.$$

Zinc oxide is reduced to the metal on heating with carbon. When zinc compounds are heated on the charcoal block in the usual way, the metal, when formed, volatilises, passes into the oxidising flame and re-forms the oxide, which appears as an incrustation.

1. Burn a small fragment of zinc on a deflagrating-spoon.
2. Treat zinc metal (2 spatula-points) with dilute hydrochloric acid ; ignite the evolved gas. The reaction may be used on a larger scale for the preparation of hydrogen (see p. 187).
3. Test the solubility of zinc hydroxide in water, dilute hydrochloric acid and sodium hydroxide.
4. Use zinc sulphate for the charcoal block test.

The fact that zinc hydroxide and carbonate are " soluble " in solutions of ammonium salts is thought to be due to the formation of a complex ion $[Zn.6NH_3]^{++}$, the hydroxide and carbonate of which are soluble in water.

The Zn^{++}, $[Zn.6NH_3]^{++}$ and ZnO_2^{--} ions are all colourless.

Solubilities of Salts.

Halides, sulphate, nitrate.   Soluble in water.

Carbonate, phosphate   .   Insoluble in water, " soluble " in dilute
                             mineral acids or in solutions of am-
                             monium salts.

Sulphide   .   .   .   Insoluble in water, " soluble " in dilute
                             mineral acids.

IONIC REACTIONS

Use zinc sulphate (0·2M solution)

No.	Reagent	Visible Result	Comments
5	**Chloride** Dil. HCl .	None.	$ZnCl_2$ is sol.
6	**Sulphide** (a) H_2S+dil. HCl . (b) H_2S+NH_4Cl +NH_4OH.	None. White ppt. ZnS.	
7	**Hydroxide** (a) NaOH . (b) NH_4OH . (c) NH_4Cl+ NH_4OH.	White ppt. $Zn(OH)_2$. ,, ,, None.	Sol. in excess ; for- mation of zincate. Sol. in excess ; formation of . [Zn.6NH_3]($OH)_2$. Formation of [Zn 6NH_3]($OH)_2$
8	**Carbonate** (a) Na_2CO_3 . (b) $(NH_4)_2CO_3$	White ppt $ZnCO_3$ (basic). ,, ,,	Insol. in excess. Sol. in excess or in NH_4Cl ; formation of [Zn.6NH_3]CO_3.
9	**Phosphate** Na_2HPO_4 .	White ppt. $Zn_3(PO_4)_2$.	

Analytical Behaviour.

Since zinc sulphide is insoluble in water but " soluble " in acids, zinc is in Class B of the Cation Separation. Since its hydroxide is " soluble " in the presence of ammonium salts, it is in Group 4.

BIOLOGICAL RÔLE AND MEDICAL USES

Zinc (in traces) is essential for human life ; it is present in the enzyme carbonic anhydrase, which catalyses the reaction $H_2CO_3 \rightleftharpoons CO_2+H_2O$ in red blood cells and other cells.

Soluble zinc compounds are astringent and are poisonous if taken

Analytical Behaviour.

Barium, like calcium, falls in Class C, Group 5, of the Cation Separation.

MEDICAL USES

Barium, having a high atomic weight, *is opaque to X-rays and is used to render the alimentary canal visible.* For this purpose the insoluble *sulphate* is used, since soluble barium salts are very toxic.

9, 16   ZINC

Valency : 2.	*Cation* : Zn^{++}.
Oxide : ZnO.	*Anion* : ZnO_2^{--}.

Zinc is a fusible metal of medium density (m.p.=420°; d=6·9), which is stable in dry air, but in moist air forms a white basic carbonate. If heated in air it burns with a bluish-white flame forming the oxide. $2Zn + O_2 = 2ZnO$.

The metal does not react with cold water, but " dissolves " readily in dilute acids, giving salts and hydrogen.

$$Zn + 2H^+ \;=\; Zn^{++} + H_2\uparrow.$$

The metal also " dissolves " in hot caustic alkalis, forming zincates (see below). $Zn + 2OH^- = ZnO_2^{--} + H_2\uparrow$.

The oxide (ZnO, white when cold, yellow when hot) and the hydroxide (Zn(OH)$_2$, white) are insoluble in water. The hydroxide is *amphoteric*. When treated with strong acids, it acts as a weak base, " dissolving " to give soluble salts in which Zn^{++} is the cation. $Zn(OH)_2 + 2H^+ = Zn^{++} + 2H_2O$. When treated with strong bases, it acts as a weak acid, " dissolving " to give soluble salts in which zinc is part of the anion (zincate ion, ZnO_2^{--}).

$$Zn(OH)_2 + 2OH^- \;=\; ZnO_2^{--} + 2H_2O.$$

Zinc oxide is reduced to the metal on heating with carbon. When zinc compounds are heated on the charcoal block in the usual way, the metal, when formed, volatilises, passes into the oxidising flame and re-forms the oxide, which appears as an incrustation.

1. Burn a small fragment of zinc on a deflagrating-spoon.
2. Treat zinc metal (2 spatula-points) with dilute hydrochloric acid; ignite the evolved gas. *The reaction may be used on a larger scale for the preparation of hydrogen* (see p. 187).
3. Test the solubility of zinc hydroxide in water, dilute hydrochloric acid and sodium hydroxide.
4. Use zinc sulphate for the charcoal block test.

The fact that zinc hydroxide and carbonate are " soluble " in solutions of ammonium salts is thought to be due to the formation of a complex ion [Zn.6NH$_3$]$^{++}$, the hydroxide and carbonate of which are soluble in water.

The Zn^{++}, [Zn.6NH$_3$]$^{++}$ and ZnO_2^{--} ions are all colourless.

Analytical Behaviour.

Since cadmium sulphide is insoluble in water and dilute acid, the metal is in Class A; since the chloride is soluble in water, the metal is in Group 2 of the Cation Separation.

9, 18   MERCURY

Valency : 2.   *Oxide :* HgO.

Cations : Hg_2^{++}, mercurous; Hg^{++}, mercuric.

Mercury is the only metal liquid at room temperature (m.p.$=-39°$; b.p.$=357°$; $d=13.6$). It is not attacked by air or oxygen, except on long heating to about 350° when it forms the oxide HgO. This oxide is decomposed on strong heating alone; $2HgO=2Hg+O_2$.

As mercury is below hydrogen in the electrochemical series it does not react with water, and dissolves only in the "oxidising acids" (compare copper). Being below copper in the electrochemical series, it is displaced from solutions of its salts by the latter.

$$Hg^{++}+Cu = Hg+Cu^{++}.$$
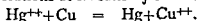
Mercuric oxide HgO, which exists in two forms, yellow and red, is insoluble in water, but "soluble" in dilute acids. The hydroxide $Hg(OH)_2$ is unknown.

Many simple compounds are volatile and sublime on heating, *e.g.*, $HgCl_2$ (white), HgI_2 (red and yellow), HgS (black and red). The oxy-salts decompose on heating, giving first mercuric oxide, then metallic mercury. All mercury compounds on heating with sodium carbonate yield metallic mercury. Since the metal is volatile, mercury compounds when heated on the charcoal block give no residue.

1. Heat mercuric oxide (1 spatula-point).
2. Heat mercury (1 drop) with concentrated sulphuric acid.
3. Dip a small strip of metallic copper into mercuric chloride solution. The strip becomes covered with a film of mercury (grey).
4, 5, 6. Heat mercuric chloride alone, with sodium carbonate in a test-tube, and on the charcoal block.

Mercury is unique among metals in forming an ion Hg_2^{++} (mercurous [1]) and compounds in which two atoms of the metal are *directly* attached to one another. Mercurous compounds, apart from the chloride Hg_2Cl_2 (calomel), are unimportant.

Both mercurous and mercuric ions are colourless. Mercuric ions may be *reduced* by stannous ions (and by some organic compounds, *e.g.*, formates, see p. 419). Stannous chloride solution reduces mercuric salts first to white insoluble mercurous chloride and then to black mercury metal:

$$2Hg^{++}+Sn^{++} \rightleftharpoons Hg_2^{++}+Sn^{++++}.$$
$$Hg_2^{++}+2Cl^- \rightleftharpoons Hg_2Cl_2\downarrow.$$
$$Hg_2Cl_2+Sn^{++} \rightleftharpoons Sn^{++++}+2Cl^-+2Hg\downarrow.$$
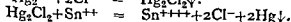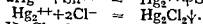
7. Treat mercuric chloride solution with stannous chloride solution.

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[1] The mercurous ion was formerly considered to be Hg^+, and the chloride to be HgCl.

in large doses ; the sulphate is used as an emetic, and the oxide and carbonate are used as mild antiseptics in ointments and lotions for external application. Zinc oxychloride is used for filling teeth.

Insulin is often administered in a form containing zinc and protamine.

9, 17   CADMIUM

Valency : 2.   *Oxide : CdO.*   *Cation : Cd++.*

Cadmium metal resembles zinc. Its oxide is brown ; its hydroxide $(Cd(OH)_2$, white) is basic, not amphoteric (contrast zinc), and forms an ammonia complex $[Cd.4NH_3](OH)_2$ soluble in water. When heated on a charcoal block, cadmium compounds give a brown incrustation of the oxide.

1. Use cadmium nitrate for the charcoal block test.

The ion Cd++ is colourless.

Solubilities of Salts.

Halides, sulphate, nitrate.	Soluble.	
Sulphide . . .	Insoluble in water, dilute acid and ammonium sulphide.	
Carbonate . . .	Insoluble in water, " soluble " in dilute acids.	

IONIC REACTIONS

Use cadmium nitrate (0·2M solution)

No.	Reagent	Visible Result	Comments
2	**Chloride** Dil. HCl . .	None.	$CdCl_2$ is sol.
3	**Sulphide** (a) H_2S+dil. HCl. (b) H_2S+NH_4Cl +NH_4OH. (c) $(NH_4)_2S_2$	}Yellow ppt. CdS.	Cd does not form a thio-salt (contrast As).
4	**Hydroxide** (a) NaOH . . (b) NH_4OH .	White ppt. $Cd(OH)_2$. ,, ,,	On heating gives brown CdO. Sol. in excess NH_4OH or in NH_4Cl; formation of $[Cd.4NH_3](OH)_2$.
5	**Carbonate** (a) Na_2CO_3 . . (b) $(NH_4)_2CO_3$	White ppt. $CdCO_3$. ,, ' ,,	Sol. in excess NH_4OH or in NH_4Cl; formation of complex.

Mercurous chloride (calomel) is insoluble in water ; on heating alone it sublimes. On heating with sodium carbonate it gives metallic mercury. On treatment with ammonium hydroxide solution it is blackened, due to the formation of ~~white HgNH₂Cl and black mercury~~ metal. $Hg_2Cl_2 + 2NH_3 = NH_4^+ + Cl$
with stannous chloride solution, it
mercury metal (see reaction 7 above).

13, 14. Heat mercurous chloride alone, and with sodium carbonate.
15. Treat mercurous chloride with dilute ammonium hydroxide.

IONIC REACTIONS

Use mercurous nitrate (0·1M solution in nitric acid)

No.	Reagent	Visible Result	Comments
16	Chloride Dil. HCl	White ppt. Hg_2Cl_2.	
17	Sulphide H_2S	Black ppt. $HgS + Hg$.	
18	Hydroxide (a) NaOH (b) NH_4OH	Black ppt. Hg_2O. Black ppt. Hg + basic salt.	
19	Carbonate Na_2CO_3	Yellow ppt. Hg_2CO_3.	

Analytical Behaviour.

Since mercurous chloride is insoluble in water, the ion is in Group 1 in the Cation Separation.

MEDICAL USES

Mercury and its compounds are used in medicine for a variety of purposes. Mercurous chloride (calomel) is used as a purgative and certain organic mercury compounds are used as diuretics. Mercuric chloride, potassium mercuri-iodide and organic mercury compounds (including phenyl mercuric nitrate) are used in very dilute solutions as antiseptics. These compounds are very toxic.

Ointments containing yellow mercuric oxide or " ammoniated mercury " ($HgNH_2Cl$) are used for external application. Mercury, mercuric chloride and organic mercuric compounds are used in the treatment of syphilis in conjunction with organic arsenic compounds.

MERCURIC SALTS

Solubilities.

Chloride, bromide, sulphate, nitrate   Soluble in water.

Iodide . . . . .   Insoluble in water and dilute acids, but " soluble " in excess iodide due to the formation of $[HgI_4]^{--}$ complex ion.

Sulphide . . . .   Insoluble in water and dilute acids.

Carbonate (basic) . . .   *Insoluble in water but " soluble " in dilute acids.*

IONIC REACTIONS

Use mercuric chloride (0·2M solution)

No.	Reagent	Visible Result	Comments
8	**Chloride** Dil. HCl . .	None.	$HgCl_2$ is sol.
9	**Sulphide** (a) H_2S+dil. HCl. (b) H_2S+NH_4Cl +NH_4OH. (c) $(NH_4)_2S_2$.	} Black ppt. HgS.	Hg does not form thio-salts (contrast As).
10	**Hydroxide** (a) NaOH . (b) NH_4OH.	Yellow ppt. HgO. White ppt.	Complex amino compound.
11	**Carbonate** (a) Na_2CO_3 . (b) $(NH_4)_2CO_3$.	Yellow ppt. White ppt.	Basic carbonate. Complex amino compound, sol. in excess $(NH_4)_2CO_3$.
12	**Iodide** KI . .	Red ppt. HgI_2.	Sol. in excess KI; formation of $[HgI_4]^{--}$.

Analytical Behaviour.

Mercuric sulphide is insoluble in water and dilute acid ; the mercuric ion is therefore in Class A in the Cation Separation. Since mercuric chloride is soluble in water, the ion is in Group 2.

MERCUROUS SALTS

The only common mercurous salt soluble in water is the nitrate $Hg_2(NO_3)_2$.

Borax on heating swells, gives off its water of crystallisation and melts to a clear liquid. If salts of other metals are heated with this liquid, the borates of the metals are formed. Since some of these borates are coloured, their formation in a "borax bead" may be used as a test for the metals concerned. Several of these metals exist in two states of oxidation, and two different borates are formed, depending on whether the bead is heated in the oxidising or the reducing flame. See tests with copper (p. 192), iron (p. 270), etc. For practical details see p. 185.

The most characteristic reaction of boric acid is the formation of esters (*e.g.*, methyl borate, $B(OCH_3)_3$) which burn with a *green* flame.

4. To borax (1 spatula-point) in a porcelain basin add concentrated sulphuric acid (10 drops) and methyl alcohol (2 ml.) and ignite.

The systematic reactions of borates are unimportant. Neither dilute hydrochloric acid nor concentrated sulphuric acid gives any visible change, although boric acid is liberated.

The borate ions are colourless.

Solubilities of Salts.

| Alkali metal salts | . | Soluble in water. |
| Other salts | . . | Mostly insoluble in water, "soluble" in dilute acids. |

IONIC REACTIONS

Use sodium pyroborate (saturated solution)

No.	Reagent	Visible Result	Comments
5	Hydrogen Dil. HCl . .	None.	Acid is stable, soluble and non-volatile.
6	Silver $AgNO_3$ . .	White ppt. Ag_3BO_3.	Sol. in dil. HNO_3.
7	Barium $Ba(NO_3)_2$ . .	White ppt. $Ba(BO_2)_2$.	Sol. in dil. HNO_3.

MEDICAL USES

Boric acid and borax are used as mild antiseptics and as neutralising agents for alkali and acid burns respectively. These compounds are dangerous if taken into the system repeatedly, and the use of boric acid as a preservative in foodstuffs is therefore prohibited.

PERIODIC GROUP III

The only important elements in this Group are boron, a non-metal which forms an acidic oxide, and aluminium, a metal which forms an amphoteric oxide. Each shows only the Group valency of 3.

· 9, 19   BORON

Valency : 3.   *Oxide :* B_2O_3.   *Anions :* BO_2^-, BO_3^{--}, $B_4O_7^{--}$.

The boric acids and their salts are the only important compounds of boron. The acids are different hydrates of the oxide B_2O_3, the commonest being H_3BO_3. It is a white solid, sparingly soluble in cold water, more soluble in hot water, and is a very weak acid, pK_a (first stage)=9·24.

The acid reacts with organic compounds containing two *adjacent* hydroxyl groups to form a stronger acid, probably as follows :

$$
\begin{array}{c}
-\text{C}-\text{OH} \quad \text{HO} \\
\qquad\qquad\qquad \rangle \text{B}-\text{OH} \\
-\text{C}-\text{OH} \quad \text{HO}
\end{array}
=
\begin{array}{c}
-\text{C}-\text{O} \\
\qquad\qquad \rangle \text{B}-\text{OH}+2\text{H}_2\text{O}. \\
-\text{C}-\text{O}
\end{array}
$$
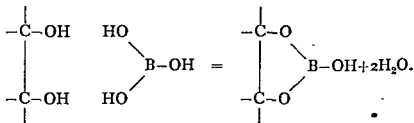
1. Test the solubility and action on litmus of boric acid.

2. To boric acid solution (2 ml.) add bromothymol blue (1 drop) and adjust the pH to 7 (colour, green) by dropwise addition of sodium carbonate solution. Add mannitol ($CH_2OH.(CHOH)_4 CH_2OH$, 2 spatula-points) ; the colour changes to yellow, *i.e.*, the pH is reduced to 6 or below. Carry out a blank test, adding mannitol to water.

Boric acid turns turmeric-paper a characteristic *red-brown colour,* which on treatment with alkali becomes greenish-black. The chemistry of the reaction is unknown.

3. Dip turmeric-paper into a solution of borax acidified with hydrochloric acid, and dry the paper by placing it on a watch-glass over the boiling water bath. When dry, add a drop of dilute sodium hydroxide.

The commonest salt is borax, sodium pyroborate, $Na_2B_4O_7$. This is a white solid, soluble in water ; it is hydrolysed in solution and may be titrated with a strong acid, using methyl red as indicator (see pp. 141 and 143).

IONIC REACTIONS

Use aluminium sulphate (0·2M solution)

No.	Reagent	Visible Result	Comments
5	**Chloride** Dil HCl . .	None.	$AlCl_3$ is sol.
6	**Sulphide** (a) H_2S+dil. HCl .	None.	Al_2S_3 is hydrolysed by water.
	(b) H_2S+NH_4Cl +NH_4OH.	White ppt. $Al(OH)_3$.	
7	**Hydroxide** (a) NaOH .	White ppt. $Al(OH)_3$.	*Sol.* in excess NaOH; formation of aluminate.
	(b) NH_4OH . .	White ppt. $Al(OH)_3$.	Insol. in excess NH_4OH or in NH_4Cl.
8	**Carbonate** Na_2CO_3 or $(NH_4)_2CO_3$.	White ppt. $Al(OH)_3$.	Aluminium carbonate does not exist.

Analytical Behaviour.

Since aluminium sulphide is hydrolysed to the hydroxide, aluminium is not precipitated in Class A (Groups 1 and 2). The hydroxide is precipitated by ammonium hydroxide and ammonium chloride and the metal is therefore in Class B, Group 3.

MEDICAL USES

Soluble aluminium salts (*e.g.*, alum and aluminium acetate) are used as astringents. Aluminium hydroxide is used as an antacid. Kaolin (*aluminium silicate*) is used as an adsorbent.

PERIODIC GROUP IV

The two "typical" elements, the non-metals carbon and silicon, are both extremely important—carbon as the basis of life, silicon as being, next to oxygen, the commonest element on the earth's surface. Both are usually quadrivalent, but the similarities between them are superficial rather than real.

Only the simplest compounds of carbon with oxygen and hydrogen are considered in this chapter. All other carbon compounds form the

ALUMINIUM

> *Valency* : 3.   *Cation* : Al+++.
> *Oxide* : Al₂O₃.   *Anion* : AlO₃---.

Aluminium is a light metal (m.p.=659°; *d*=2·7). It is apparently unaffected by air, but probably becomes covered with a thin transparent film of the oxide, which prevents further oxidation. On heating in air, it burns with a white flame, forming the oxide Al_2O_3.

Aluminium does not react with cold water, but "dissolves" in dilute hydrochloric or sulphuric acid with evolution of hydrogen.

$$2Al + 6H^+ = 2Al^{+++} + 3H_2\uparrow.$$
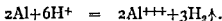
Nitric acid appears to have no effect on the metal; it is thought that an impermeable layer of oxide is formed on the surface. Aluminium "dissolves" in caustic alkalis with evolution of hydrogen.

$$2Al + 6OH^- = 2AlO_3^{---} + 3H_2\uparrow.$$
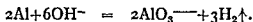
Aluminium is a powerful reducing agent, reducing many other metallic oxides to metals (Thermite process—not safe for students' experiment). The oxide Al_2O_3 cannot be reduced by carbon, and therefore remains as a residue when aluminium compounds are submitted to the charcoal block test.

The oxide Al_2O_3 and hydroxide $Al(OH)_3$ (both white) are insoluble in water. The hydroxide is *amphoteric* and therefore "dissolves" both in dilute acids (*giving* Al+++ *salts*) *and in dilute caustic alkalis*, giving aluminates (AlO₃--- ion). Aluminium does *not* form a complex ion with ammonia (contrast zinc).

1. Burn a small piece of aluminium foil.

2, 3. Treat aluminium with dilute hydrochloric acid and with dilute sodium hydroxide.

4. Use aluminium sulphate for the charcoal block test.

The ions Al+++ and AlO₃--- are both colourless.

Solubilities of Salts.

Halides, sulphate, nitrate.			Soluble in water.
Sulphide	.	.	Hydrolysed by water to the hydroxide and hydrogen sulphide.
Carbonate	.	.	Does not exist.
Phosphate	.	.	Insoluble in water, "soluble" in dilute mineral acids or caustic alkalis.

B. The metallic carbonate is decomposed by heat, giving the oxide.

$$CuCO_3 = CuO + CO_2.$$
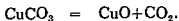
C. The metallic oxide is reduced by charcoal to the metal.

$$CuO + C = Cu + CO.$$

The following variations may occur :

  (i) *Alkali metals.* Reaction *A* only occurs, since the alkali metal carbonates are stable.

  (ii) *Alkaline earth metals, magnesium and aluminium.* Reactions *A* and *B* only occur, since the metallic oxides are not reduced by carbon.

  (iii) *Volatile metals* (zinc, arsenic, cadmium—also bismuth, lead, antimony). Reactions *A*, *B*, and *C* occur, but the metal, being volatile, passes into the oxidising flame and is re-oxidised. An "incrustation" of oxide is therefore formed on the charcoal block. With zinc, arsenic and cadmium compounds, all the metal is reoxidised thus. With bismuth, lead, and antimony compounds, only part of the metal is reoxidised.

Carbon reduces concentrated sulphuric acid to sulphur dioxide on heating. $C + 2H_2SO_4 = CO_2 + 2SO_2 + 2H_2O.$

3. Heat graphite with concentrated sulphuric acid ; note the smell of sulphur dioxide.

HYDRIDES OF CARBON

Carbon forms a great number of hydrides, consideration of which is really the province of the organic chemist. Three simple hydrides or *hydrocarbons,* normally included in inorganic chemistry courses, are treated here. These are :

methane CH_4 (a paraffin or saturated hydrocarbon) ;
ethylene C_2H_4 ($H_2C:CH_2$, an olefin or unsaturated hydrocarbon) [1] ;
acetylene C_2H_2 (HC : CH, a doubly-unsaturated hydrocarbon).

These hydrocarbons are all colourless gases, insoluble in water. They may be prepared as follows :

Methane. By decarboxylation of sodium acetate on heating with soda-lime.

$$CH_3.COONa + NaOH = Na_2CO_3 + CH_4.$$
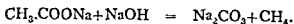
Ethylene. By removal of the elements of water from ethyl alcohol by concentrated sulphuric acid.

$$H_3C.CH_2OH - H.OH = H_2C:CH_2.$$
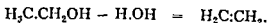
[1] Ethylene is sometimes used as an anaesthetic.

province of the organic chemist, and are treated in Part Five of this book.

The two metals of the B Subgroup included here, tin and lead, show valencies of 2 and 4, and form amphoteric oxides.

9, 21   CARBON

Valency : 4.

Hydrides : CH_4, C_2H_4, C_2H_2, etc.

Oxides : CO, CO_2.

Anions : CO_3^{--}, carbonate ; CN^-, cyanide ; OCN^-, cyanate ; SCN^-, thiocyanate.

Charcoal and graphite, the two most common forms of carbon, are both black solids, insoluble in water and all aqueous solvents, infusible and non-volatile. Charcoal is porous and hence has a large surface area. It is used in the laboratory as an adsorbent for gases and for dissolved substances (see p. 121). It is also used in medicine as an adsorbent for undesirable materials (gaseous or dissolved) in the alimentary canal. Graphite has a layer-structure (pp. 82-84) ; it cleaves readily and is therefore used as a lubricant and in lead pencils. It is a metallic conductor.

Charcoal and graphite burn on heating in air or oxygen, giving carbon monoxide or dioxide, according to the amount of oxygen available.

$$2C + O_2 = 2CO ; C + O_2 = CO_2.$$

1, 2. Ignite charcoal and graphite in turn in a deflagrating-spoon, placing the spoon in a boiling-tube while the solid is burning ; keep the gaseous products for reactions.

The *reactions of carbon with hydrogen and the halogens cannot be carried out here*. Carbon combines with some metals to give carbides.[1]

Carbon is a powerful reducing agent. Most metallic oxides (except the alkalis and alkaline earths) are reduced to metal on heating with carbon. This reaction forms the basis of the *charcoal block tests*. In these tests, a salt or oxide is heated with charcoal and sodium carbonate on a charcoal block in the reducing flame (for practical instructions see p. 185). The following reactions take place with a typical salt (*e.g.*, cupric sulphate) :

A. The salt reacts with sodium carbonate to give the carbonate of the metal and the sodium salt of the anion.

$$CuSO_4 + Na_2CO_3 = CuCO_3 + Na_2SO_4.$$

The sodium sulphate melts and is absorbed by the charcoal.

---

[1] These are *not* salts. Except for calcium carbide (p. 214) they are not considered here.

9. *Fume Cupboard.* Prepare carbon monoxide by adding concentrated sulphuric acid (5 ml.) to sodium formate (5 spatula-points). Gas Apparatus, Type B 1. Show that the gas is almost insoluble in water.

10. Show that carbon monoxide burns with a blue flame.

CARBON DIOXIDE AND CARBONIC ACID

Carbon dioxide (CO_2) is a colourless gas, denser than air, with a faint characteristic smell. It is present in the air (about 0·03% by volume) and dissolves in water, forming some carbonic acid (see below). It does not support combustion. It is prepared by acting on any carbonate with a dilute mineral acid.

$$CaCO_3 + 2HCl = CaCl_2 + CO_2 + H_2O.$$
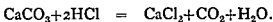
or 3 marble chips),
.). (Gas Apparatus,
Use two tubes for
solubility of carbon
2 drops) and shake ;

12. Show that carbon dioxide is not inflammable and does not support combustion.
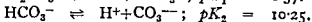
The gas is recognised by its reaction with calcium hydroxide to give calcium carbonate—it " turns lime water milky."
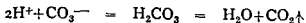
$$CO_2 + Ca(OH)_2 = CaCO_3 \downarrow + H_2O.$$

This reaction is considered further below. The test for carbon dioxide may be applied as follows :

13. Take in a *dry boiling-tube* sodium carbonate (1 spatula-point). Add slowly dilute hydrochloric acid (5 drops). Take a drop of clear lime water on the end of a glass-rod and lower this into the tube *without knocking the drop off.* The drop becomes milky.

Carbonic acid (H_2CO_3) exists only in solution. It is very unstable and on formation breaks down almost completely at room temperature to give carbon dioxide and water. It is a very weak dibasic acid dissociating in two stages thus :
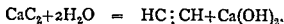
$$H_2CO_3 \rightleftharpoons H^+ + HCO_3^-\ ;\ pK_1 = 6·37.$$
$$HCO_3^- \rightleftharpoons H^+ + CO_3^{--}\ ;\ pK_2 = 10·25.$$

Carbonic acid is weaker than all the inorganic acids included in this book (except H_2S, HCN, H_3AsO_3 and $HClO$), and weaker than many organic acids (*e.g.*, acetic acid). It is displaced from its salts by any stronger acid, and immediately decomposes, carbon dioxide being evolved as a gas.

$$2H^+ + CO_3^{--} = H_2CO_3 = H_2O + CO_2 \uparrow$$

(see reactions 11 and 13 above).

Acetylene. By the action of water on calcium carbide.

$$CaC_2 + 2H_2O = HC \colon CH + Ca(OH)_2.$$

The three gases are all highly inflammable, burning in air to give carbon dioxide and water. If pure the gases burn smoothly on ignition; if mixed with air, they explode on ignition. Coal gas contains about 25% by volume of methane.

Methane is rather inert, and reacts with the halogens slowly by substitution thus:

$$CH_4 + Cl_2 = CH_3Cl + HCl.$$

Ethylene and acetylene are reactive and combine immediately with the halogens by addition thus:

$$C_2H_4 + Br_2 = C_2H_4Br_2.$$
$$C_2H_2 + 2Br_2 = C_2H_2Br_4.$$

4. Prepare methane by heating together sodium acetate (anhydrous, 4 spatula-points) and soda-lime (4 spatula-points). Gas Apparatus, Type A 1. Show that the gas is almost insoluble in water.

5. Prepare ethylene by heating together ethyl alcohol (5 ml.) and concentrated sulphuric acid (5 ml.). Gas Apparatus, Type B 1. Show that the gas is almost insoluble in water.

6. Prepare acetylene by treating calcium carbide (4 spatula-points) with water (10 ml.). Gas Apparatus, Type B 1. Show that the gas is almost insoluble in water.

7. Examine the behaviour of the three hydrocarbons when ignited (a) pure, (b) mixed with air.

8. Bubble each of three hydrocarbons through bromine water (5 ml.). Ethylene and acetylene decolorise the reagent rapidly, and the addition compounds (heavy oily liquids) sink to the bottom of the water. Methane does not react appreciably with the reagent.
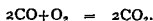

CARBON MONOXIDE

Carbon monoxide (CO) is a colourless gas, which does not dissolve in or react with water and is neutral to indicators. It is very poisonous, since it combines with the haemoglobin of the blood and interferes with respiration (see pp. 412-413). It must *not* be inhaled. Coal gas contains 5-10% carbon monoxide; the unburnt gas, and the partly-burnt gas from a " lit-back " Bunsen burner, are therefore dangerous.

Carbon monoxide may be prepared by the dehydration of formic acid by concentrated sulphuric acid.

$$H.COOH = H_2O + CO.$$

Carbon monoxide burns with a blue flame, forming carbon dioxide.

$$2CO + O_2 = 2CO_2.$$

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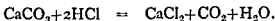
⸱⸱ ⸱⸱⸱⸱⸱ ⸱⸱ ⸱⸱⸱ ⸱⸱⸱⸱⸱ ⸱ ⸱ ⸱⸱⸱⸱ ⸱ ⸱ ⸱ ⸱⸱ ⸱ or 3 marble chips),
⸱⸱⸱⸱⸱). (Gas Apparatus,
Use two tubes for
solubility of carbon
dioxide in water. To another tube add litmus solution (2 drops) and shake; the litmus is turned reddish-purple.

12. Show that carbon dioxide is not inflammable and does not support combustion.

The gas is recognised by its reaction with calcium hydroxide to give calcium carbonate—it "turns lime water milky."

$$CO_2 + Ca(OH)_2 \rightleftharpoons CaCO_3\downarrow + H_2O.$$

This reaction is considered further below. The test for carbon dioxide may be applied as follows:

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(see reactions 11 and 13 above).

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$$CaC_2 + 2H_2O = HC \vdots CH + Ca(OH)_2.$$

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5. Prepare ethylene by heating together ethyl alcohol (5 ml.) and concentrated sulphuric acid (5 ml.). Gas Apparatus, Type B 1. Show that the gas is almost insoluble in water.

6. Prepare acetylene by treating calcium carbide (4 spatula-points) with water (10 ml.). Gas Apparatus, Type B 1. Show that the gas is almost insoluble in water.

7. Examine the behaviour of the three hydrocarbons when ignited (a) pure, (b) mixed with air.

8. Bubble each of three hydrocarbons through bromine water (5 ml.). Ethylene and acetylene decolorise the reagent rapidly, and the addition compounds (heavy oily liquids) sink to the bottom of the water. Methane does not react appreciably with the reagent.

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Carbon monoxide may be prepared by the dehydration of formic acid by concentrated sulphuric acid.

$$H.COOH = H_2O + CO.$$

Carbon monoxide burns with a blue flame, forming carbon dioxide.

$$2CO + O_2 = 2CO_2.$$

Some carbonates "dissolve" in water containing carbon dioxide to give soluble bicarbonates.

$$CaCO_3 + CO_2 + H_2O \ = \ Ca^{++} + 2HCO_3^-.$$
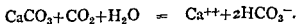
19. Bubble carbon dioxide through lime water (5 ml.). The lime water first becomes milky, *i.e.*, calcium carbonate is precipitated. It then clears as this dissolves, forming bicarbonate.

The solutions of normal carbonates are alkaline to all common indicators, due to hydrolysis ; the solutions of bicarbonates are alkaline to bromophenol blue or methyl orange, faintly alkaline to bromothymol blue or litmus, and neutral to phenolphthalein.

IONIC REACTIONS

Use sodium carbonate (0.2M solution)

No.	Reagent	Visible Result	Comments
20	Hydrogen Dil. HCl	CO_2 given off.	Acid is weak and unstable.
21	Silver $AgNO_3$	White ppt. Ag_2CO_3.	Sol. in dil. HNO_3 with effervescence.
22	Barium $Ba(NO_3)_2$	White ppt. $BaCO_3$.	Sol. in dil. HNO_3 with effervescence.
23	Calcium $CaCl_2$	White ppt. $CaCO_3$.	Sol. in dil. HNO_3 with effervescence.

BIOLOGICAL RÔLE AND MEDICAL USES

Carbon dioxide is produced in tissues by the oxidation of organic compounds with the liberation of energy. In animals with a blood system (including man) the carbon dioxide is transported away from the tissues by the blood and liberated in the lungs (or corresponding organs). The bicarbonate-carbon dioxide system plays an important part in buffering the pH of ..... (Human plasma normally cont

C. acids ; they have the disadvantage that carbon dioxide is produced when they neutralise acid in the stomach.

HYDROCYANIC ACIDS AND CYANIDES

Hydrocyanic acid and cyanides are very poisonous. Hydrocyanic acid, which is volatile, must not be inhaled, and cyanogen compounds must not be allowed to touch the mouth or hands. Reactions of the cyanides should

The acid salts, bicarbonates, *e.g.*, NaHCO₃, in solutions of which the ion HCO_3^- exists, are important. They are unstable to heat, all being decomposed on boiling their aqueous solutions. (They can be distinguished from normal carbonates by this property.) Sodium, potassium and ammonium bicarbonates alone exist as solids. Calcium, barium, magnesium and ferrous bicarbonates exist in solution.

All bicarbonates, all normal carbonates (*except* those of sodium and potassium) and all basic carbonates are decomposed with varying ease on heating to give carbon dioxide and a metallic oxide.

$$CaCO_3 \ = \ CaO + CO_2.$$
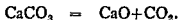
The normal carbonates of sodium and potassium are *not* decomposed on heating.

14, 15, 16. Heat in turn sodium bicarbonate, magnesium carbonate and sodium carbonate (2 spatula-points each) and confirm the above statements.

Many water-insoluble and acid-insoluble salts may be brought into solution by fusion with sodium carbonate (or sodium carbonate + potassium carbonate, "fusion mixture") or by boiling with saturated aqueous sodium carbonate solution. The reaction with, *e.g.*, magnesium phosphate is as follows :

$$Mg_3(PO_4)_2 + 3Na_2CO_3 \ = \ 2Na_3PO_4 + 3MgCO_3.$$

If the boiling saturated solution is filtered or the fusion product extracted with hot water and filtered, the original anions (*e.g.*, phosi . . . . be identi-
. . . . e present
. . . . in dilute hydrochloric acid, giving the soluble chlorides of the cations, which may then be identified.

17. Fuse in a nickel crucible calcium phosphate (2 spatula-points) and fusion mixture (10 spatula-points). Cool, extract the product with boiling water (10 mL.) and filter. Test the filtrate for phosphate (molybdate test, p. 236). Dissolve in dilute acetic acid the material insoluble in water. Show that the resulting solution gives the reactions for calcium (oxalate)..

18. Boil together for 5 minutes in a small beaker barium sulphate (2 spatula-points) and saturated sodium carbonate solution (10 mL.). Filter and test the filtrate and precipitate for sulphate and barium respectively.

Both carbonate CO_3^- and bicarbonate HCO_3^- ions are colourless.

Solubilities of Salts.

Carbonates of sodium, potassium and ammonium } Soluble in water.
All bicarbonates .   .   .   .   .   .   }

All other carbonates and basic carbonates.   .   Insoluble in water, "soluble" in dilute acids.

Solubilities of Salts.

Sodium, potassium, ammonium, calcium, barium, mercuric.	Soluble in water.
All others	Insoluble in water; many "soluble" in alkali cyanide solutions due to complex formation.

IONIC REACTIONS

Use potassium cyanide (0·2M solution).   *Fume Cupboard*

No.	Reagent	Visible Result	Comments
27	Hydrogen Dil. HCl .	HCN evolved.	Test by formation of thiocyanate (reaction 24 above).
28	Silver AgNO₃ . .	White ppt. AgCN.	Insol. in HNO₃, sol. in excess KCN; formation of K[Ag(CN)₂].
29	Barium Ba(NO₃)₂ . .	None.	Ba(CN)₂ is sol.

THIOCYANATES

Thiocyanates (*e.g.*, KSCN) are used in volumetric analysis for the determination of silver, and hence indirectly of halides (see pp. 150-152). The name "thiocyanate" is derived from that of cyanates (*e.g.*, KOCN), which will not be met in elementary courses.

The reaction between thiocyanates and concentrated sulphuric acid is complicated. Carbon dioxide, sulphur dioxide, and carbon oxysulphide (COS) are evolved, and sulphur is precipitated.

30. Heat potassium thiocyanate ($\frac{1}{4}$ spatula-point) with concentrated sulphuric acid.

The ion SCN⁻ is colourless; the salts are all soluble in water except those of silver, mercury, copper and lead—compare solubilities of chlorides.

Ferric iron gives with thiocyanate a r . . . . . . colour[1] due to complex ferri- . . . . . . " . . . . . ly important reactions of thio- . . . . . . : . . . r nitrate and ferric chloride.

[1] The red colour was formerly thought to be due to unionised ferric thiocyanate Fe(SCN)₃.

be carried out in a fume cupboard under the direct supervision of a demonstrator. Cyanide residues must be made alkaline and poured down the sink with much water.

Hydrocyanic acid ("prussic acid" HCN) is very weak (pK_a=9·14), weaker even than carbonic acid; the carbon dioxide of the air therefore displaces it from its salts, which always smell of the free acid (bitter-almond smell), and are contaminated with carbonates. Dilute hydrochloric acid liberates the acid from its salts (reactions 24 and 27).

The acid and its salts resemble the halogen hydracids (HCl, etc.) and their salts in many ways. A striking difference, however, lies in the *number* and *stability* of the *complex salts* formed. Many very stable complex cyanides exist (*e.g.*, ferrocyanides and ferricyanides, see reaction 26 and pp. 273–274); complex halides are less common, and usually less stable. The acid is oxidised by ammonium polysulphide to thiocyanic acid HSCN, which gives a characteristic red colour with ferric chloride (see p. 219). This reaction provides a *safe* test for hydrocyanic acid.

$$HCN + S = HSCN.$$
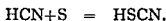
The acid is the *nitrile* of formic acid (see pp. 418–419). If a cyanide is heated with concentrated sulphuric acid, the following reactions take place:

(*a*) Liberation of hydrocyanic acid.
$$KCN + H_2SO_4 = HCN + KHSO_4.$$

(*b*) Hydrolysis of hydrocyanic acid to formic acid.
$$HCN + 2H_2O = HCOOH + NH_3.$$
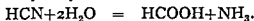
(*c*) Dehydration of formic acid to carbon monoxide.
$$HCOOH - HOH = CO.$$

Cyanides react in alkaline solution with ferrous salts to form ferrocyanides, which give a characteristic precipitate or colour of Prussian blue on the addition of a ferric salt.

$$Fe^{++} + 6CN^- = [Fe(CN)_6]^{----}.$$

24. *(Fume Cupboard.)* Soak a strip of filter-paper in ammonium polysulphide

25. *(Fume Cupboard.)* Heat potassium cyanide (½ spatula-point) with
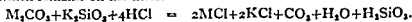
The cyanide ion is colourless.

is a mixture of silicates (and often borates), soft glass being a sodium calcium silicate, and hard glass a potassium calcium silicate. The chemistry of silicates is almost a science of its own, and cannot be treated adequately in an elementary course.

Silicon carbide (SiC, carborundum) is used for grinding and polishing glass (e.g., for bevelling the stems of funnels).

1. *Preparation of a Solution from an Insoluble Silicate.* Take the silicate

$$M_2SiO_3 + K_2CO_3 = M_2CO_3 + K_2SiO_3.$$

Cool, add concentrated hydrochloric acid (2 ml.), boil and filter. The metals are turned into their soluble chlorides, while the silicate radicals form silicic acid which remains on the filter.

$$M_2CO_3 + K_2SiO_3 + 4HCl = 2MCl + 2KCl + CO_2 + H_2O + H_2SiO_3.$$

2. *Distinction between Soft and Hard Glass.* Heat the ends of two pieces of glass rod—one hard, the other soft—in the hottest part of the Bunsen flame. The soft glass gives a sodium (yellow) flame and melts readily. The hard glass gives a faint potassium (lilac) flame and hardly melts at all.

IONIC REACTIONS

Use sodium silicate (0·2M solution)

No.	Reagent	Visible Result	Comments
3	Hydrogen Dil. HCl	White gelatinous * ppt. H_2SiO_3.	Acid is weak and sparingly sol.
4	Silver $AgNO_3$	Orange ppt. Ag_2SiO_3.	Sol. in dil. HNO_3.†
5	Barium $Ba(NO_3)_2$	White ppt. $BaSiO_3$.	Sol. in dil. HNO_3.†

* The acid may sometimes remain in colloidal solution.
† Insoluble silicic acid may be formed.

MEDICAL USES

Kaolin is an aluminium silicate which is used as an adsorbent in medicine. Talc is a " layer silicate " (see pp. 82-84) which is used as an anti-irritant in dusting powders.

9, 23   **TIN**

Valencies : 2, 4.   *Cations* : Sn^{++}, stannous ; Sn^{+++}, stannic.
Oxides : SnO, SnO_2.   *Anions* : SnO_2^{--}, stannite ; SnO_3^{--}, stannate.

Tin is a fusible heavy white metal (m.p.=232° ; d=7·2), which is stable in air. It does not react with water but " dissolves " in acids.

IONIC REACTIONS

Use potassium thiocyanate (0·2M solution)

No.	Reagent	Visible Result	Comments
31	**Hydrogen** Dil. HCl . .	None.	
32	**Silver** AgNO₃ . .	White ppt. AgSCN.	Insol. in HNO₃.
33	**Barium** Ba(NO₃)₂ . .	None.	Ba(SCN)₂ is sol.
34	**Ferric** FeCl₃ . .	Red colour, due to [Fe(SCN)₆]⁻.	

OTHER CARBON COMPOUNDS

Carbon disulphide CS_2 is a volatile, poisonous, *very inflammable* liquid (b.p.=46°; d=1·26). It may be met as a solvent for sulphur. It must be kept away from naked flames.

Carbon tetrachloride CCl_4 is an inert liquid (b.p.=77°; d=1·60) which is a non-electrolyte. It is insoluble in, and does not react with, water or alkali (contrast most other non-metal halides).

35. Show that carbon tetrachloride is insoluble in water, gives no precipitate with silver nitrate solution, and is unaffected by boiling with sodium hydroxide (contrast chloroform $CHCl_3$, p. 416).

Carbon tetrachloride is a good solve~~ⁿᵗ~~ f~~....~~ ~~.. ..   .. ..~~ ~~.......~~ and for the halogens (see bromine, p. ~~.~~ ·   ~~.   .~~ ~~:~~ in medicine as an anthelmintic, *i.e.,* ~~:~~   ~~:~~ ~~.:~~

9, 22   SILICON

Valency: 4.   *Oxide:* SiO_2.   *Anions:* $SiO_3{}^{--}$ and many complexes.

The element silicon is unimportant. Its oxide (silicon dioxide, SiO_2, silica) is a colourless solid of very high melting-point, insoluble in water and hardly attacked by any aqueous solutions. Silica vessels are therefore used for work with many reagents which would attack glass. Sand consists mainly of silica.

Silicic acids (various hydrates of silica) are very weak acids. They may be insoluble in water or may form colloidal solutions. All silicates except those of sodium and potassium are insoluble in water, and most of them can be brought into aqueous solution only by fusion with alkali carbonates. Many rocks and clays consist of silicates—sometimes pure substances, more often very complex mixtures. Glass
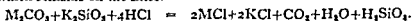
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2. *Distinction between Soft and Hard Glass.* Heat the ends of two pieces of glass rod—one hard, the other soft—in the hottest part of the Bunsen flame. The soft glass gives a sodium (yellow) flame and melts readily. The hard glass gives a faint potassium (lilac) flame and hardly melts at all.

IONIC REACTIONS

Use sodium silicate (0·2M solution)

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3	Hydrogen Dil. HCl	White gelatinous * ppt. H_2SiO_3.	Acid is weak and sparingly sol.
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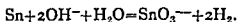
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34	Ferric FeCl₃ . . .	Red colour, due to [Fe(SCN)₆]‴.	

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35. Show that carbon tetrachloride is insoluble in water, gives no precipitate with silver nitrate solution, and is unaffected by boiling with sodium hydroxide (contrast chloroform $CHCl_3$, p. 416).

Carbon tetrachloride is a good solvent for many organic compounds and for the halogens (see bromine, p. 262; iodine, p. 264). It is used in medicine as an anthelmintic, *i.e.*, to destroy intestinal parasites.

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Silicon carbide (SiC, carborundum) is used for grinding and polishing glass (*e.g.*, for bevelling the stems of funnels).

1. *Preparation of a Solution from an Insoluble Silicate.* Take the silicate (1 spatula-point) fusion mixture ($Na_2CO_3 + K_2CO_3$, 6 spatula-points) and fuse in a nickel crucible. The metals originally present as silicates are turned into their carbonates thus (M=a univalent metal).

$$M_2SiO_3 + K_2CO_3 \ = \ M_2CO_3 + K_2SiO_3.$$

Cool, add concentrated hydrochloric acid (2 ml.), boil and filter. The metals are turned into their soluble chlorides, while the silicic radicals form silicic acid which remains on the filter.

$$M_2CO_3 + K_2SiO_3 + 4HCl \ = \ 2MCl + 2KCl + CO_2 + H_2O + H_2SiO_3.$$

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Oxides : SnO, SnO_2.   *Anions* : SnO_2^{--}, stannite ; SnO_3^{--}, stannate.

Tin is a fusible heavy white metal (m.p.=232° ; d=7·2), which is stable in air. It does not react with water but "dissolves" in acids.

Hydrochloric acid gives stannous chloride and hydrogen: $Sn+2H^+=Sn^{++}+H_2\uparrow$. Concentrated nitric acid reacts vigorously, giving hydrated stannic oxide (SnO_2) and reduction products of the acid. The metal also "dissolves" in hot caustic alkalis, giving a stannate and hydrogen.

$$Sn+2OH^-+H_2O=SnO_3^{--}+2H_2.$$

Stannous oxide SnO is black and stannic oxide SnO_2 is white. The corresponding hydroxides $Sn(OH)_2$ and $Sn(OH)_4$ are both white solids insoluble in water, and *amphoteric*. Stannous hydroxide "dissolves" in acids to give stannous salts, *e.g.*, $SnCl_2$(Sn^{++} ion), and in caustic alkalis to give stannites, *e.g.*, Na_2SnO_2(SnO_2^{--} ion). Stannic hydroxide gives similarly stannic salts, *e.g.*, $SnCl_4$ (Sn^{++++} ion), and stannates, *e.g.*, Na_2SnO_3 (SnO_3^{--} ion).

Stannous and stannic salts are all hydrolysed by water to give insoluble basic salts, which "dissolve" on treatment with a strong acid.

All tin compounds are reduced to the metal when heated on the charcoal block.

1, 2, 3. Examine the behaviour of tin with hydrochloric acid (1 volume concentrated acid+1 volume water), concentrated nitric acid, and hot dilute sodium hydroxide.

4. Use stannic oxide for the charcoal block test.

Stannous salts are *reducing agents*, and stannic salts *oxidising agents* (although the latter are rarely used as such).

$$Sn^{++} \rightleftharpoons Sn^{++++}+2e.$$

Stannous salts are oxidised by

(a) mercuric salts (see p. 205);

(b) dichromates in acid solution, these being reduced to green chromic salts;

(c) permanganates in acid solution, these being reduced to almost colourless manganous salts.

5. Examine the behaviour of stannous chloride with the oxidising agents listed above.

Both stannous and stannic sulphides react with ammonium polysulphide to form a soluble *thiostannate*, the stannous salt being oxidised by the "extra" sulphur in the polysulphide solution.

$$SnS_2+S^{--} = SnS_3^{--}$$
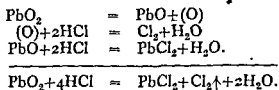$$SnS+S^{--}+S = SnS_3^{--}.$$

All the tin ions considered here are colourless.

Stannous salts are more common than stannic; the only stannic compounds considered here are the chloride, oxide and sulphide.

STANNOUS SALTS

Solubilities.

Chloride, bromide, sulphate, nitrate.	React with water to give insoluble basic salts, but "dissolve" in the presence of a strong acid.
Iodide	Sparingly soluble in water even in the presence of dilute acids, but readily "soluble" in iodide solutions.
Sulphide . . .	Insoluble in water and cold dilute acids.
Carbonate . . .	Does not exist.

IONIC REACTIONS

Use stannous chloride (0·2M solution in hydrochloric acid)

No.	Reagent	Visible Result	Comments
6	**Chloride** Dil. HCl . .	None.	$SnCl_2$ is sol.
7	**Sulphide** (a) H_2S+dil HCl .	Brown ppt. SnS.	Ppt. is sol. in $(NH_4)_2S_2$; formation of thiostannate.
	(b) H_2S+NH_4Cl +NH_4OH.	,, ,,	
8	**Hydroxide** (a) NaOH .	White ppt. $Sn(OH)_2$.	On heating gives black SnO. $Sn(OH)_2$ is sol. in excess NaOH, giving a stannite.
	(b) NH_4OH .	White ppt. $Sn(OH)_2$.	Insol. in excess NH_4OH or in NH_4Cl.
9	**Carbonate** Na_2CO_3 or $(NH_4)_2CO_3$.	White ppt. $Sn(OH)_2$.	$SnCO_3$ does not exist.

Analytical Behaviour.

Since stannous sulphide is insoluble in water and in dilute acids, the ion is in Class A in the Cation Separation. Since the chloride is soluble (in presence of acid), the ion is in Group 2.

STANNIC SALTS

Stannic chloride $SnCl_4$ is a colourless liquid. It is hydrolysed by water to stannic hydroxide and hydrochloric acid, and fumes in moist air.

$$SnCl_4 + 4HOH = Sn(OH)_4 + 4HCl\uparrow.$$

Hydrochloric acid gives stannous chloride and hydrogen: $Sn + 2H^+ = Sn^{++} + H_2\uparrow$. Concentrated nitric acid reacts vigorously, giving hydrated stannic oxide (SnO_2) and reduction products of the acid. The metal also "dissolves" in hot caustic alkalis, giving a stannate and hydrogen.

$$Sn + 2OH^- + H_2O = SnO_3^{--} + 2H_2.$$

Stannous oxide SnO is black and stannic oxide SnO_2 is white. The corresponding hydroxides $Sn(OH)_2$ and $Sn(OH)_4$ are both white solids insoluble in water, and *amphoteric*. Stannous hydroxide "dissolves" in acids to give stannous salts, *e.g.*, $SnCl_2(Sn^{++}$ ion), and in caustic alkalis to give stannites, *e.g.*, $Na_2SnO_2(SnO_2^{--}$ ion). Stannic hydroxide gives similarly stannic salts, *e.g.*, $SnCl_4$ (Sn^{++++} ion), and stannates, *e.g.*, Na_2SnO_3 (SnO_3^{--} ion).

Stannous and stannic salts are all hydrolysed by water to give insoluble basic salts, which "dissolve" on treatment with a strong acid.

All tin compounds are reduced to the metal when heated on the charcoal block.

1, 2, 3. Examine the behaviour of tin with hydrochloric acid (1 volume concentrated acid + 1 volume water), concentrated nitric acid, and hot dilute sodium hydroxide.

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Stannous salts are *reducing agents*, and stannic salts *oxidising agents* (although the latter are rarely used as such).

$$Sn^{++} \quad \rightleftharpoons \quad Sn^{++++} + 2e.$$

Stannous salts are oxidised by

(a) mercuric salts (see p. 205);

(b) dichromates in acid solution, these being reduced to green chromic salts;

(c) permanganates in acid solution, these being reduced to almost colourless manganous salts.

5. Examine the behaviour of stannous chloride with the oxidising agents listed above.

Both stannous and stannic sulphides react with ammonium polysulphide to form a soluble *thiostannate*, the stannous salt being oxidised by the "extra" sulphur in the polysulphide solution.

$$SnS_2 + S^{--} = SnS_3^{--}$$
$$SnS + S^{--} + S = SnS_3^{--}.$$

All the tin ions considered here are colourless.

Stannous salts are more common than stannic; the only stannic compounds considered here are the chloride, oxide and sulphide.

acid and readily " soluble " in dilute nitric acid. The corresponding hydroxide, $Pb(OH)_2$ (white), is amphoteric; it is insoluble in water, but " dissolves " in acids and alkalis to give lead salts (plumbous Pb^{++} ion) and plumbites (PbO_2^{--} ion) respectively.

. . forms two peroxides. Pb . . O . (red lead) and PbO_2 (lead peroxide . . . . . e oxidising agents. On strong . . . . Each of these compounds is . . . . much dilute hydrochloric acid, giving lead chloride and chlorine. For the sake of writing equations, it is convenient to look upon PbO_2 as PbO plus one " oxidising " oxygen atom. Pb_3O_4 may similarly be considered as 3PbO plus one " oxidising " oxygen atom. The reaction between lead peroxide and hydrochloric acid may be represented as follows :

$$
\begin{aligned}
PbO_2 &= PbO+(O) \\
(O)+2HCl &= Cl_2+H_2O \\
PbO_2+2HCl &= PbCl_2+H_2O.
\end{aligned}
$$

$$\overline{PbO_2+4HCl = PbCl_2+Cl_2{\uparrow}+2H_2O.}$$

Lead compounds when heated on a charcoal block are reduced to metallic lead ; since the metal is somewhat volatile, an incrustation of oxide is also formed.

1. Treat a small piece of granulated lead with concentrated nitric acid.

2. Heat lead peroxide alone

3. Warm (a) red lead, (b) lead peroxide (¼ spatula-point each) with dilute hydrochloric acid (5 ml.)

4. Use lead monoxide for the charcoal block test.

The lead ion Pb^{++} and the plumbite ion PbO_2^{--} are both colourless.

Solubilities of Salts.

Nitrate, acetate [1]	.	Soluble in water.
Halides . .	.	All sparingly soluble in cold water (particularly the iodide), but moderately soluble in hot water ; these salts are no more soluble in dilute acids than in water.
Sulphate, sulphide	.	Insoluble in water and in dilute acids.
Carbonate .	.	Insoluble in water, sparingly " soluble " in dilute hydrochloric acid, readily " soluble " in dilute nitric acid.

[1] $(CH_3COO)_2Pb$. Commonly used as a source of Pb^{++} ions.

It therefore resembles the non-metal halides (*e.g.*, phosphorus pentachloride). Stannic chloride dissolves in hydrochloric acid; the solution gives the reactions of the stannic ion.

Stannic sulphide is a yellow solid, insoluble in water and dilute acids.

IONIC REACTIONS

Use stannic chloride (0·2M solution in hydrochloric acid)

No.	Reagent	Visible Result	Comments
10	**Chloride** Dil. HCl . .	None.	
11	**Sulphide** (*a*) H$_2$S+dil. HCl. (*b*) H$_2$S+NH$_4$Cl +NH$_4$OH.	} Yellow ppt. SnS$_2$.	Sol. in (NH$_4$)$_2$S or (NH$_4$)$_2$S$_3$; formation of thiostannate.
12	**Hydroxide** (*a*) NaOH .	White ppt. Sn(OH)$_4$.	Sol. in excess NaOH; formation of stannate.
	(*b*) NH$_4$OH. .	„ „	Insol. in excess NH$_4$OH or NH$_4$Cl.
13	**Carbonate** Na$_2$CO$_3$ or (NH$_4$)$_2$CO$_3$.	White ppt. Sn(OH)$_4$.	Sn(CO$_3$)$_2$ does not exist.

Analytical Behaviour.

The same as that of the stannous ion.

9, 24   LEAD

Valencies : 2, 4.   *Cation* : Pb++.
Oxides : PbO, Pb$_3$O$_4$, PbO$_2$.   *Anion* : PbO$_2$⁼.

Lead is a heavy soft fusible metal (m.p.=326° ; d=11·3), which oxidises only superficially in air at ordinary temperatures. On heating in air it forms the monoxide PbO. It is not appreciably affected by water or by inorganic acids other than the " oxidising acids." Nitric acid dissolves it, giving lead nitrate and nitrogen peroxide.

$$Pb+4HNO_3 = Pb(NO_3)_2+2NO_2+2H_2O.$$
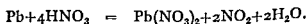
The normal oxide PbO (lead monoxide, litharge) is yellow or pink, and is insoluble in water, sparingly " soluble " in dilute hydrochloric

PERIODIC GROUP V

The typical and B Subgroup elements alone are important, viz. nitrogen, phosphorus, arsenic, antimony and bismuth. All show both Group valencies of 3 and 5. This family illustrates very well decrease of electronegative character from the elements of small weight (nitrogen and phosphorus, non-metals, forming acidic oxides), through the intermediate elements (arsenic and antimony, metalloids, forming amphoteric oxides), to the element of largest atomic weight (bismuth, metal, forming a basic oxide). Special mention must be made of ammonia (NH_3) as the only hydride which is *basic* in character.

Many organic compounds of nitrogen are of great physiological importance. Some of these are considered in Part Five of this book.

9, 25 **NITROGEN**

Valencies : 3, 5.
Hydride : NH_3.
Oxides : N_2O, NO, N_2O_3, NO_2, N_2O_5.
Cation : NH_4^+, ammonium.
Anions : NO_2^-, nitrite ; NO_3^-, nitrate.

Nitrogen N_2 is a colourless, odourless gas, sparingly soluble in water. It may be prepared by heating a solution of ammonium nitrite.

$$NH_4NO_2 \rightleftharpoons N_2 + 2H_2O.$$
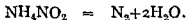
Nitrogen is a very unreactive substance and is recognised by its inactivity in all the tests used. It does not support combustion or react with lime water. (Contrast carbon dioxide which is also a non-supporter of combustion.) Nitrogen forms about four-fifths (by volume) of the atmosphere.

1. *Preparation of Nitrogen.* Gas Apparatus, Type B 1. Dissolve in water

2, 3. Show that a burning splint and burning sulphur are extinguished when plunged into nitrogen.

4. Show the nitrogen does not turn lime water milky.

AMMONIA, AMMONIUM SALTS

Ammonia, NH_3, is a colourless gas of characteristic smell, lighter than air, and is a non-supporter of combustion. It is extremely soluble in water. Some dissolved ammonia reacts with water to give

IONIC REACTIONS

Use lead acetate (0·2M solution)

No.	Reagent	Visible Result	Comments
5	**Chloride** Dil. HCl . .	White ppt. $PbCl_2$.	In fairly conc. solns. only; ppt. is sol. in hot water.
6	**Sulphide** (a) H_2S+dil. HCl. (b) H_2S+NH_4Cl +NH_4OH.	} Black ppt. PbS.	
7	**Hydroxide** (a) NaOH . .	White ppt. $Pb(OH)_2$.	Sol. in excess NaOH; formation of plumbite.
	(b) NH_4OH . .	White ppt. $Pb(OH)_2$.	Insol. in excess NH_4OH or in NH_4Cl.
8	**Carbonate** Na_2CO_3 or $(NH_4)_2CO_3$.	White ppt. $PbCO_3$ (basic).	
9	**Iodide** KI . . .	Yellow ppt. PbI_2.	Sparingly sol. in hot water.
10	**Sulphate** Dil. H_2SO_4 . .	White ppt. $PbSO_4$.	
11	**Chromate** K_2CrO_4 . .	Yellow ppt. $PbCrO_4$.	

Analytical Behaviour.

Since the sulphide is insoluble in water and dilute acid, lead is in Class A of the Cation Separation. Since the chloride *is slightly soluble in water*, lead may appear *either* in Group 1 (precipitation of lead chloride from concentrated solutions) *or* Group 2 (precipitation of lead sulphide from dilute solutions).[1]

MEDICAL USES

Lead, like other heavy metals, is an astringent; the acetate is used for this purpose. Lead is a cumulative poison if taken into the system.

[1] Lead is the *only* element which may appear in two different groups in the Cation Separation.

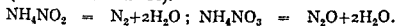and the acid. In most cases further reactions then take place. The final results may be classified as follows :

(a) If the acid is non-volatile and stable, ammonia is evolved and the acid remains behind; no further reaction takes place. Example, ammonium phosphate.

$$(NH_4)_2HPO_4 = 2NH_3 + H_2O + HPO_3.$$

(b) If the acid is volatile, it is evolved together with the ammonia, and if the mixture is cooled the two recombine. If the salt is heated in a test-tube a "sublimate" of the salt is formed in the higher part of the tube; this decomposition and recombination is *not* true sublimation. Example, ammonium chloride.

$$NH_4Cl \rightleftharpoons NH_3 + HCl.$$

(c) If the acid is an oxidising agent, it oxidises the hydrogen of the ammonia, being itself reduced. Examples, ammonium nitrite and nitrate (see reactions 1 and 16).

$$NH_4NO_2 = N_2 + 2H_2O ; NH_4NO_3 = N_2O + 2H_2O.$$

Ammonia and ammonium salts give, with potassium mercuri-iodide (K_2HgI_4) in alkaline solution (Nessler's reagent), a brown colour or precipitate (formula uncertain). This test is very sensitive and is used for the colorimetric determination of ammonia in solution (see pp. 70-71).

10, 11. Heat ammonium phosphate and ammonium chloride.

12. To Nessler's reagent (2 ml.) add 1 drop of 0.01M ammonium hydroxide solution (prepared by diluting 1 drop of 2M solution to 10 ml. with distilled water).

The ammonium ion is colourless.

Solubilities of Salts.

The ammonium salts of all common inorganic acids are soluble in water. A few rare ammonium salts are sparingly soluble, including the cobaltinitrite and acid tartrate (compare potassium, p. 191).

IONIC REACTIONS

Use ammonium chloride (0·2M solution)

No.	Reagent	Visible Result	Comments
13	Hydroxide NaOH.	NH₃ evolved.	Smell, test with litmus-paper.
14	Cobaltinitrite Na₃[Co(NO₂)₆]	Yellow ppt. (NH₄)₃[Co(NO₂)₆].	
15	Acid Tartrate NaH.C₄H₄O₆	White ppt. NH₄.H.C₄H₄O₆.	

ammonium hydroxide,[1] which is a *weak* base ionising slightly as follows (pK_b=4·75).

$$NH_3+H_2O \;\rightleftharpoons\; NH_4OH \;\rightleftharpoons\; NH_4^++OH^-.$$

On heating in solution ammonium hydroxide decomposes completely to give ammonia and water. Ammonia is the *only* non-metallic hydride which is the anhydride of a base, and therefore is the *only* inorganic gas which turns moist litmus-paper blue.

Ammonia and ammonium hydroxide combine with acids to give salts which are *strong* electrolytes ; the salts are partly hydrolysed in water, since ammonium hydroxide is a weak base (see pp. 95-96).

$$NH_4OH+H^++Cl^- \;=\; NH_4^++Cl^-+HOH.$$

Since ammonium hydroxide is a weak, unstable base giving rise to a volatile decomposition product, it is easily displaced from its salts by strong bases in the cold.

$$NH_4^+(+Cl^-+K^+)+OH^- \;=\; NH_4OH(+K^++Cl^-) \;=\; NH_3+H_2O.$$

This reaction is used for the identification of ammonium salts in qualitative analysis, and also for the quantitative determination of ammonia (see pp. 145-148).

A 3. Heat ammonium
tubes of gas. Use one

is extinguished.

8. Hold a glass rod moistened with concentrated hydrochloric acid at the

white solid.

The compounds of the ammonium ion are in many ways similar to those of sodium and potassium. The chief differences are as follows :

(1) Ammonium hydroxide is a *weak* base while sodium and potassium hydroxides are *strong*.

(2) Ammonia forms with many metallic ions *complex ions* of the type $[Ag.2NH_3]^+$, whose properties, and in particular the solubilities of whose salts, are often very different from those of the simple ions ; hence the " solubility " of salts such as silver chloride in ammonium hydroxide.

The facts (1) and (2) together account for the wide differences in behaviour of many cations with *sodium* hydroxide and carbonate on the one hand, and with *ammonium* hydroxide and carbonate on the other.

(3) All ammonium salts on heating dissociate, giving at first ammonia

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[1] The aqueous solution is called sometimes " ammonia," sometimes " ammonium hydroxide " ; each name is partly correct. The " concentrated ammonia " of the laboratory (d=0·880) contains about 300 g. NH_3 per litre and is about 15M.

and the acid. In most cases further reactions then take place. The final results may be classified as follows :

(a) If the acid is non-volatile and stable, ammonia is evolved and the acid remains behind; no further reaction takes place. Example, ammonium phosphate.

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No.	Reagent	Visible Result	Comments
13	Hydroxide NaOH.	NH_3 evolved.	Smell, test with litmus-paper.
14	Cobaltinitrite $Na_3[Co(NO_2)_6]$	Yellow ppt. $(NH_4)_3[Co(NO_2)_6]$.	
15	Acid Tartrate $NaH.C_4H_4O_6$	White ppt. $NH_4 H C_4H_4O_6$.	

Analytical Behaviour.

Since all common ammonium salts are soluble in water, the ion is in Class C, Group 6 of the Cation Separation.

OXIDES OF NITROGEN

Nitrogen forms five oxides and two oxyacids. The two oxides which are anhydrides of the oxyacids (N_2O_3 and N_2O_5) cannot be studied in an elementary class.

Nitrogen trioxide (N_2O_3) is a blue liquid at temperatures below $0°$, which decomposes at room te————————————————————— peroxide. It is the anhydride responsible for the fleeting solution of a nitrite is acidified (see reaction 26).

Nitrogen pentoxide (N_2O_5) is the anhydride of nitric acid, HNO_3.

NITROUS OXIDE

Nitrous oxide, N_2O, is a colourless gas with a characteristic smell; it is moderately soluble in water, with which it does not react. It may be prepared by heating ammonium nitrate gently.

$$NH_4NO_3 = N_2O + 2H_2O.$$

Nitrous oxide supports combustion, though less vigorously than oxygen; *e.g.*, $2N_2O + S = SO_2 + 2N_2$. It does *not* oxidise an alkaline solution of pyrogallol (contrast oxygen).
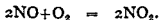
Nitrous oxide is used as an anaesthetic in minor surgery and dentistry.

16. *Preparation.* Gas Apparatus, Type A 1. Heat gently ammonium nitrate (3 g.). Collect two and a half tubes of gas. Use the half-tube to show the solubility of the gas in water.
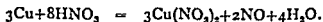
17, 18. Examine the behaviour of a glowing splint and burning sulphur in the gas.

NITRIC OXIDE

Nitric oxide, NO, is a colourless gas, sparingly soluble in water, with which it does not react. On contact with air or oxygen it reacts immediately, forming brown nitrogen peroxide.
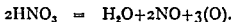
$$2NO + O_2 = 2NO_2.$$

The gas is prepared by the action of moderately concentrated nitric acid on copper.
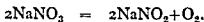
$$3Cu + 8HNO_3 = 3Cu(NO_3)_2 + 2NO + 4H_2O.$$

Nitric oxide often plays a part similar to that played by ammonia and water in the formation of complex ions. The " brown ring " formed in testing for nitrites and nitrates (see reactions 25 and 31) is due to a co-ordination compound of ferrous iron with nitric oxide, $Fe(NO)SO_4$. Another co-ordination compound containing nitric oxide is sodium nitroprusside $Na_2[Fe(CN)_5(NO)]$.

19. *Preparation.* Gas Apparatus, Type B 1. Treat copper turnings (3 g.) with a mixture of concentrated nitric acid (5 ml.) and water (5 ml.). Collect two and a half tubes of gas. Use the half-tube to show the sparing solubility of the gas with water.

20. Show that nitric oxide when exposed to air forms brown nitrogen peroxide.

21. Show that nitric oxide gives a brown colour with ferrous sulphate solution.

NITROGEN PEROXIDE

Nitrogen peroxide or dioxide is a heavy brown gas with a characteristic smell. At ordinary temperature it is a mixture of NO_2 and N_2O_4 molecules. The gas dissolves readily in water, giving a mixture of nitrous and nitric acids (*i.e.*, it is a " mixed anhydride ").

$$N_2O_4 + H_2O = HNO_2 + HNO_3.$$
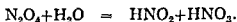
It is formed by the thermal decomposition of nitric acid and nitrates, and by the reduction of concentrated nitric acid by copper.

$$Cu + 4HNO_3 = 2NO_2 + Cu(NO_3)_2 + 2H_2O.$$

22. *Preparation.* Gas Apparatus, Type B 2. Treat copper turnings (3 g.) with concentrated nitric acid (5 ml.). Collect four tubes of gas. Use two tubes for a density comparison and a third tube to show the solubility of the gas in water.

NITROUS ACID AND NITRITES

Nitrous acid HNO_2 is a weak acid, and is unstable, breaking down on formation at room temperature as follows :

$$2HNO_2 = N_2O_3 + H_2O = NO_2 + NO + H_2O.$$
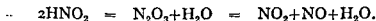
Dilute mineral acids or acetic acid liberate nitrous acid from its salts, and it then decomposes (see reaction 26).

Nitrites act sometimes as reducing agents and sometimes as oxidising agents. As reducing agents they are oxidised to nitrates, *e.g.*, by permanganates.

$$NO_2^- + (O) = NO_3^-.$$
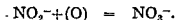
Nitrites oxidise iodides in acidified solutions to iodine, being themselves reduced to nitric oxide.

$$2HNO_2 = 2NO + H_2O + (O).$$
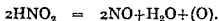
On heating alone, all nitrites except those of sodium, potassium and ammonium give off brown fumes of nitrogen peroxide. Ammonium nitrite (in solution) decomposes to give nitrogen (see p. 227) ; sodium and potassium nitrites are stable to heat.

If a faintly acidified solution of ferrous sulphate is added to a nitrite solution, the nitric oxide formed by decomposition of the liberated nitrous acid forms with ferrous sulphate a dark brown addition compound $Fe(NO)SO_4$. Some other anions give dark-brown colours in the conditions of this test or of the related test for nitrates (see p. 233) ;

Analytical Behaviour.

Since all common ammonium salts are soluble in water, the ion is in Class C, Group 6 of the Cation Separation.

OXIDES OF NITROGEN

Nitrogen forms five oxides and two oxyacids. The two oxides which are anhydrides of the oxyacids (N_2O_3 and N_2O_5) cannot be studied in an elementary class.

Nitrogen trioxide (N_2O_3) is a blue liquid at temperatures below 0°, which decomposes at room temperature to nitric oxide and nitrogen peroxide. It is the anhydride of HNO_2, nitrous acid, and is probably responsible for the fleeting pale-blue colour formed when a cold solution of a nitrite is acidified (see reaction 26).

Nitrogen pentoxide (N_2O_5) is the anhydride of nitric acid, HNO_3.

NITROUS OXIDE

Nitrous oxide, N_2O, is a colourless gas with a characteristic smell; it is moderately soluble in water, with which it does not react. It may be prepared by heating ammonium nitrate gently.

$$NH_4NO_3 = N_2O + 2H_2O.$$

Nitrous oxide supports combustion, though less vigorously than oxygen; *e.g.*, $2N_2O + S = SO_2 + 2N_2$. It does *not* oxidise an alkaline solution of pyrogallol (contrast oxygen).

Nitrous oxide is used as an anaesthetic in minor surgery and dentistry.

16. *Preparation.* Gas Apparatus, Type A 1. Heat gently ammonium nitrate (3 g.). Collect two and a half tubes of gas. Use the half-tube to show the solubility of the gas in water.

17, 18. Examine the behaviour of a glowing splint and burning sulphur in the gas.

NITRIC OXIDE

Nitric oxide, NO, is a colourless gas, sparingly soluble in water, with which it does not react. On contact with air or oxygen it reacts immediately, forming brown nitrogen peroxide.

$$2NO + O_2 = 2NO_2.$$

The gas is prepared by the action of moderately concentrated nitric acid on copper.

$$3Cu + 8HNO_3 = 3Cu(NO_3)_2 + 2NO + 4H_2O.$$

Nitric oxide often plays a part similar to that played by ammonia and water in the formation of complex ions. The "brown ring" formed in testing for nitrites and nitrates (see reactions 25 and 31) is due to a co-ordination compound of ferrous iron with nitric oxide, $Fe(NO).SO_4$. Another co-ordination compound containing nitric oxide is sodium nitroprusside $Na_2[Fe(CN)_5(NO)]$.

with excess of ferrous sulphate to give a brown complex Fe(NO)SO$_4$.
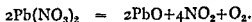
$$2HNO_3 = H_2O + 2NO + 3(O).$$

With a nitrite, a trace of hydrogen ion is sufficient to liberate nitrous acid, which immediately decomposes, giving nitrogen peroxide and nitric oxide, the latter then combining with ferrous sulphate. In the case of a nitrate *concentrated sulphuric acid* is necessary to liberate nitric acid, which is then reduced to nitric oxide by ferrous sulphate. All other anions must have been proved absent before this reaction can be used as a test for nitrate.

On heating alone alkali metal nitrates yield the nitrite and oxygen.

$$2NaNO_3 = 2NaNO_2 + O_2.$$

Most other nitrates on heating yield nitrogen peroxide, oxygen and the oxide of the metal.

$$2Pb(NO_3)_2 = 2PbO + 4NO_2 + O_2.$$

29. Heat sodium nitrate with concentrated sulphuric acid.

30. Heat sulphur with concentrated nitric acid. Test the product for sulphate ions with barium nitrate.

31. *Brown Ring Test.* Mix ferrous sulphate and sodium nitrate solutions (1 ml. of each) and layer the mixture on to concentrated sulphuric acid. (See p. 33.) A brown or purple ring is formed at the interface.

32. Heat sodium nitrate; test the evolved gas with a glowing splint and the residue with dilute hydrochloric acid.

33. Heat lead nitrate. Note the brown fumes evolved.

The nitrate ion is colourless. The salts are *all soluble* in water—except that the bismuth, arsenic, antimony and tin salts are hydrolysed to basic nitrates, which are insoluble in water, but " soluble " in dilute nitric acid.

Precipitation tests cannot be used for the identification of this ion.

OTHER NITROGEN COMPOUNDS

Hydroxylamine NH$_2$OH and *hydrazine* H$_2$N.NH$_2$ (or derivatives thereof) will be met in organic chemistry (see pp. 330-332 and 384-386). The *halogen compounds* of nitrogen are not important.

9, 26   **PHOSPHORUS**

Valencies : 3, 5.   *Hydride* : PH$_3$.   *Oxides* : P$_2$O$_3$, P$_2$O$_5$.
Anions : PO$_3^-$, PO$_4^{--}$, P$_2$O$_7^{--}$; meta-, ortho- and pyro-phosphate.

The element phosphorus exists in several allotropic solid forms. The yellow form is very active and is not suitable for students' use. The red form is less active and may be used to illustrate some reactions. Red phosphorus is an odourless solid, which is insoluble in and does not react with water. It burns in air or oxygen, giving the pentoxide
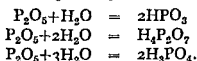
all other anions must therefore be proved absent before these tests are done.

23. Show that sodium nitrite solution decolorises an acidified permanganate solution.

24. Show that sodium nitrite solution blackens starch-iodide paper which has been dipped in dilute acid.

25. Add to sodium nitrite solution a solution of ferrous sulphate containing acetic acid.

The nitrite ion is colourless. All metallic nitrites are soluble in water (the silver salt sparingly).

IONIC REACTIONS

Use sodium nitrite (0·2M solution)

No.	Reagent	Visible Result	Comments
26	Hydrogen Dil. HCl . .	Brown gas, NO_2, given off.	
27	Silver $AgNO_3$ . .	White ppt. $AgNO_2$.	In very conc. soln. only; $AgNO_2$ is fairly sol.
28	Barium $Ba(NO_3)_2$ . .	None.	$Ba(NO_2)_2$ is sol.

NITRIC ACID AND NITRATES

Nitric acid, HNO_3, is a colourless liquid; its solution in water is a strong acid. The acid is therefore not displaced from its salts by hydrochloric acid. The usual " conc. HNO_3 " of the laboratory is an aqueous solution containing about 70% HNO_3 by weight. This solution is colourless when pure, but is usually coloured yellow by decomposition products. The acid decomposes as follows on heating strongly:

$$4HNO_3 = 4NO_2 + O_2 + 2H_2O.$$
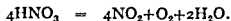
Since the acid is volatile, it is liberated from its salts by concentrated ʻ‸ʼ ‸ . ʻʼ‸ . ʻ᷀ . [‸ ᷀‸‸᷀ ‸᷀‸᷀᷀ ‸᷀᷀᷀ᷕᷕᷕᷕ ᷀‸ ᷀᷀᷀‸᷀ ᷀‸᷀‸᷀‸᷀‸‸᷀ their ᷀᷀ ᷀ ᷀᷀ᷕ ʻᷕᷕᷕᷕᷕᷕᷕᷕᷕᷕᷕᷕᷕ ᷕ ᷀᷀ ‸᷀ ᷀᷀᷀ᷕ ᷀ᷕ ᷀᷀᷀ n the electrochemical series, by oxidising the hydrogen which is first formed. The acid is reduced to a variety of products; see reactions with ᷀ᷕᷕ᷀᷀᷀᷀᷀᷀᷀ ᷀᷀᷀ᷕ ᷀᷀᷀ᷕ᷀᷀ᷕ ᷀᷀ᷕᷕ᷀ᷕᷕᷕᷕ ᷀᷀᷀ᷕᷕ ᷀᷀ᷕ ᷀᷀᷀ᷕᷕ ᷀᷀᷀ᷕ᷀ᷕ

combines with excess of ferrous sulphate to give a brown complex compound $Fe(NO)SO_4$.

$$2HNO_3 = H_2O + 2NO + 3(O).$$

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P_2O_5. Phosphorus combines with chlorine and bromine to give halides (see p. 262). It reacts with sodium hydroxide to give an inflammable hydride phosphine PH_3 and a salt sodium hypophosphite NaH_2PO_2. These compounds will not be studied here.
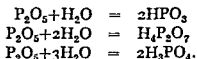
The lower oxide of phosphorus, P_2O_3, phosphorous acid, H_3PO_3, and its salts (e.g., Na_2HPO_3) are unimportant, and are not treated here.
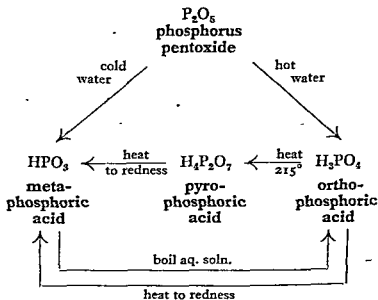
PHOSPHORIC ACIDS AND PHOSPHATES

Phosphorus pentoxide (P_2O_5, a white solid) is the anhydride of three different phosphoric acids. It is the most powerful drying and dehydrating agent known; it is used for drying many gases and organic solvents, and in desiccators.

The three acids, HPO_3, $H_4P_2O_7$ and H_3PO_4, called meta-, pyro- and ortho-phosphoric acids respectively, may be considered as formed from their common anhydride, P_2O_5, by the addition of one, two and three molecules of water respectively.

$$P_2O_5 + H_2O = 2HPO_3$$
$$P_2O_5 + 2H_2O = H_4P_2O_7$$
$$P_2O_5 + 3H_2O = 2H_3PO_4.$$

The interconversions of the acids are summed up in the following table:

P_2O_5
phosphorus
pentoxide

cold water   hot water

$HPO_3 \xleftarrow{\text{heat to redness}} H_4P_2O_7 \xleftarrow[215°]{\text{heat}} H_3PO_4$

meta-phosphoric acid   pyro-phosphoric acid   ortho-phosphoric acid

boil aq. soln.

heat to redness

2, 3. Prepare meta- and ortho-phosphoric acids by adding phosphorus pentoxide (½ spatula-point) to cold and hot water (1 ml.).

The acids are all white, odourless solids, readily soluble in water. They are weak acids ; pK_a values for ortho-phosphoric acid are 2·12, 7·21, 12·30 for the three stages of dissociation.

In conditions of fair competition phosphoric acid is displaced from its salts by strong acids. Since it is soluble, stable and non-volatile, no visible change takes place when a phosphate is treated with a strong acid, e.g., dilute hydrochloric acid (reaction 8) or concentrated sulphuric acid.

All the three phosphate ions are stable at room temperature, and may be distinguished[1] by certain tests. (See table on p. 236 and note that meta-phosphates coagulate albumin in the presence of dilute acetic acid, while ortho- and pyro-phosphates do not.) In other reactions, however, all three kinds of phosphates behave alike.

The ortho- and pyro-acids, being polybasic, form several different series of salts.

The names given to the sodium salts of ortho-phosphoric acid, and the reactions of their solutions to the common indicators, are summarised in the following table. The ordinary " sodium phosphate " of the laboratory is Na_2HPO_4.

Formula	Name	Reactions to Indicators		
		Bromo-phenol blue or methyl-orange	Bromo-thymol blue or litmus	Phenol-phthalein
Na_3PO_4	Tertiary sodium phosphate or tri-sodium phosphate.	Alkaline.	Alkaline.	Alkaline.
Na_2HPO_4	Secondary sodium phosphate or di-sodium hydrogen phosphate.	,,	,,	Neutral.
NaH_2PO_4	Primary sodium phosphate or sodium di-hydrogen phosphate or acid sodium phosphate.	Neutral.	Acidic.	Acidic.

Most phosphates are stable to heat ; some, however, lose water on heating—e.g., Na_2HPO_4 forms the pyrophosphate, and microcosmic salt $NaNH_4HPO_4$ forms sodium metaphosphate.

$$2Na_2HPO_4 = Na_4P_2O_7 + H_2O$$
$$NaNH_4HPO_4 = NaPO_3 + NH_3 + H_2O.$$
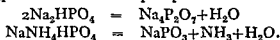
4. Heat Na_4HPO_4 with concentrated sulphuric acid.

5, 6. Heat Na_2HPO_4 and $NaNH_4HPO_4$ alone.

All the various phosphate ions are colourless.

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[1] Contrast the arsenates (see p. 240), where the three different ions are interconverted in solution so easily that it is impossible to distinguish between them and the chromates and dichromates (pp. 254-255), which are interconvertible under the influence of acid or alkali.

P_2O_5. Phosphorus combines with chlorine and bromine to give halides (see p. 262). It reacts with sodium hydroxide to give an inflammable hydride phosphine PH_3 and a salt sodium hypophosphite NaH_2PO_2. These compounds will not be studied here.

1. Ignite red phosphorus (1 spatula-point) on a deflagrating-spoon and lower it while burning into a boiling-tube. Dissolve the white fumes produced in water (2 ml.) and show that the solution is acid.

The lower oxide of phosphorus, P_2O_3, phosphorous acid, H_3PO_3, and its salts (e.g., Na_2HPO_3) are unimportant, and are not treated here.

PHOSPHORIC ACIDS AND PHOSPHATES

Phosphorus pentoxide (P_2O_5, a white solid) is the anhydride of three different phosphoric acids. It is the most powerful drying and dehydrating agent known; it is used for drying many gases and organic solvents, and in desiccators.

The three acids, HPO_3, $H_4P_2O_7$ and H_3PO_4, called meta-, pyro- and ortho-phosphoric acids respectively, may be considered as formed from their common anhydride, P_2O_5, by the addition of one, two and three molecules of water respectively.

$$P_2O_5 + H_2O = 2HPO_3$$
$$P_2O_5 + 2H_2O = H_4P_2O_7$$
$$P_2O_5 + 3H_2O = 2H_3PO_4.$$

The interconversions of the acids are summed up in the following table:

$$P_2O_5$$
phosphorus
pentoxide

cold water ↙   ↘ hot water

HPO_3 ←$\dfrac{\text{heat}}{\text{to redness}}$← $H_4P_2O_7$ ←$\dfrac{\text{heat}}{215°}$← H_3PO_4

meta-   pyro-   ortho-
phosphoric   phosphoric   phosphoric
acid   acid   acid

boil aq. soln.

heat to redness

2, 3. Prepare meta- and ortho-phosphoric acids by adding phosphorus pentoxide (¼ spatula-point) to cold and hot water (1 ml.).

in combination with sugars and organic bases in nucleoproteins; they are also present in certain other proteins (e.g., caseinogen, see p. 414). The hard matter of bones and teeth consists essentially of calcium phosphate.

The element (yellow form) is poisonous if taken internally and causes severe burns if allowed to ignite in contact with the skin.

ARSENIC
9, 27

Valencies : 3, 5.   Cation : As^{+++}.

Hydride : AsH$_3$.   Anions : AsO$_3$$^{---}$, arsenite ;

Oxides : As$_2$O$_3$, As$_2$O$_5$.   AsO$_4$$^{---}$, arsenate.

Arsenic is probably the best example of a metalloid, an element which is half metal, half non-metal, forms an amphoteric oxide and can be readily transformed from a cation into an anion and vice versa. Its compounds are well-known as poisons, though their importance for this reason is often over-emphasised. The only reaction of the element which need be considered here is its oxidation by hypochlorites to arsenate (see reaction 1).

ARSINE

Arsine (AsH$_3$) is a colourless, very poisonous gas whose formation from all arsenic compounds by reduction with nascent hydrogen forms the basis of one of the best known tests for traces of arsenic (Marsh's test).

$$As_2O_3 + 12(H) = 3H_2O + 2AsH_3.$$
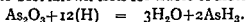
Arsine burns with a mauve flame and is decomposed by heat to arsenic and hydrogen. It reduces silver nitrate to metallic silver. (This reaction forms the basis of Gutzeit's test.)
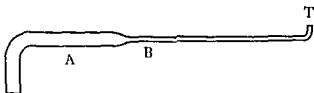
FIG. 9, 1

Tube for Marsh's Test

1, 2. Marsh's Test (simplified) and Gutzeit's Test (Fume Cupboard). Take in a test-tube zinc [1] (2 pieces), copper sulphate (2 drops), dilute sulphuric acid (10 ml.); hydrogen is evolved. Add arsenious chloride (0·1 ml. of 0·01M solution) and cork the tube with a cork carrying a hard-glass tube shaped as Fig. 9, 1. After a minute ignite the gas at the tip T. It burns with a mauve flame. Now heat the tube at the point A. A mirror of arsenic is formed at B.

Take the cork out of the test-tube and hold over the mouth of the tube a filter-paper soaked in silver nitrate solution. The paper is turned yellow and then black.

Basify the residue in the test-tube with sodium carbonate solution and pour it down the sink with much water.

Take the hard-glass tube and show that the mirror of arsenic is dissolved by sodium hypochlorite solution (oxidation to sodium arsenate).

[1] All reagents must be arsenic-free.

A most important reaction of all phosphates is the formation of a yellow insoluble complex phosphomolybdate, $(NH_4)_3PO_4, 12MoO_3$, with ammonium molybdate on gentle warming in nitric acid solution.

7. To sodium phosphate solution (10 drops) add concentrated nitric acid (1 ml.) and ammonium molybdate reagent (5 ml.) and warm gently. A yellow precipitate is formed.

Solubilities of Salts.

All sodium, potassium and ammonium salts.	Soluble in water.
All other salts (except a few acid ortho-phosphates).	Insoluble in water, but " soluble " in dilute acids.

IONIC REACTIONS

Use sodium phosphates (0·1M solutions)

No.	Reagent	Visible Results		
		Orthophosphate	Meta-phosphate	Pyrophosphate
8	**Hydrogen** Dil. HCl	None.	None.	None.
9	**Silver** AgNO₃	Yellow ppt. Ag_3PO_4 sol. in dil. HNO_3.	White ppt. $AgPO_3$ sol. in dil. HNO_3.	White ppt. $Ag_4P_2O_7$ sol. in dil. HNO_3.
10	**Barium** Ba(NO₃)₂	White ppt. sol. in dil. acetic acid.	No ppt.	White ppt. insol. in dil. acetic acid.
11	**Magnesium** MgCl₂, NH₄Cl +NH₄OH.	White ppt. $MgNH_4PO_4$ insol. in excess reagent.	No ppt.	White ppt. sol. in excess reagent.

OTHER PHOSPHORUS COMPOUNDS

The halides and oxyhalides (*e.g.*, PCl_3, PCl_5, $POCl_3$) are much used in organic chemistry for the substitution of halogen for hydroxyl radicals. These compounds are hydrolysed by water, *e.g.*,

$$PCl_5 + 4HOH = H_3PO_4 + 5HCl\uparrow$$
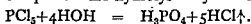
12. To phosphorus pentachloride (¼ spatula-point) add water (1 drop) and note the vigorous evolution of hydrogen chloride.

BIOLOGICAL RÔLE

The phosphoric acids in combination with various organic hydroxy compounds as esters play a most important rôle in the intermediary metabolism of carbohydrates and fats. Phosphoric acids are present

Use arsenious chloride (0·2M solution in hydrochloric acid)

No.	Reagent	Visible Result	Comments
10	Chloride Dil. HCl	None.	
11	Sulphide (a) H_2S+dil. HCl . (b) H_2S+NH_4Cl +NH_4OH.	Yellow ppt. As_2S_3.	Ppt. is sol. in $(NH_4)_2S_2$ formation of thioarsenate.
12	Hydroxide (a) NaOH . (b) NH_4OH .	White ppt. As_2O_3. ,, ,,	Ppt. in conc. solns. only. Sol. in excess of NaOH or NH_4OH due to formation of arsenite.
13	Carbonate Na_2CO_3 or $(NH_4)_2CO_3$.	White ppt. As_2O_3.	

Analytical Behaviour.

Since arsenious sulphide is insoluble in water and in dilute acid, the ion is in Class A in the Cation Separation. Since the chloride is soluble (in the presence of acid) the ion is in Group 2.

Use sodium arsenite (0·2M solution)

No.	Reagent	Visible Result	Comments
14	Hydrogen Dil. HCl	None (except in very conc. solns.)	H_3AsO_3 is weak but fairly sol.
15	Silver $AgNO_3$	Pale yellow ppt. Ag_3AsO_3.	Sol. in dil. HNO_3.
16	Barium $Ba(NO_3)_2$	White ppt. $Ba_3(AsO_3)_2$.	Sol. in dil. HNO_3.
17	Cupric $CuSO_4$	Green ppt. $CuHAsO_3$	See reaction 9 above.

ARSENIOUS COMPOUNDS

Arsenious oxide (As_2O_3), a white volatile poisonous solid, is ampho-teric. It is sparingly soluble in water, giving a solution of arsenious acid. $As_2O_3 + 3H_2O = 2H_3AsO_3$. It is readily " soluble " in caustic alkalis, giving arsenites. $As_2O_3 + 6OH^- = 2AsO_3^{---} + 3H_2O$. The oxide is also " soluble " in hydrochloric acid, giving a solution of arsenious chloride. $As_2O_3 + 6HCl = 2AsCl_3 + 3H_2O$.

Arsenic trichloride ($AsCl_3$) is a colourless oily liquid which is hydrolysed by water to arsenious oxide, $2AsCl_3 + 3H_2O = As_2O_3 + 6HCl$, but dissolves in concentrated hydrochloric acid, giving a solution which contains As^{+++} ions.

3, 4, 5. Test the solubility of arsenious oxide in water, dilute sodium hydroxide and dilute hydrochloric acid.

6, 7. Test the behaviour of arsenic trichloride (2 drops each test) with water and dilute hydrochloric acid.

Arsenite anions AsO_3^{---} and arsenious cations As^{+++} may be changed into one another at will, thus :

$$AsO_3^{---} \underset{OH^-}{\overset{H^+}{\rightleftharpoons}} As(OH)_3 \underset{OH^-}{\overset{H^+}{\rightleftharpoons}} As^{+++}.$$

in alkaline   in acid
solution   solution
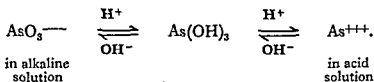
Since arsenious oxide or hydroxide is somewhat soluble in water, it is not precipitated on the neutralisation of arsenious salt or arsenite solutions, unless these are concentrated.

All arsenic compounds are reduced on the charcoal block to metal, which, being volatile, passes into the oxidising flame and forms the oxide (smell of garlic, white incrustation).

8. Heat sodium arsenite on the charcoal block.

Both arsenious salts and arsenites are recognised in qualitative analysis by the precipitation of yellow arsenious sulphide by hydrogen sulphide in acid solution (see reaction 11).

$$2As^{+++} + 3S^{--} = As_2S_3.$$

Arsenious sulphide is " soluble " in ammonium sulphide or poly-sulphide solution due to the formation of a thioarsenite or thioarsenate.

$$As_2S_3 + 3S^{--} = 2AsS_3^{---}$$
$$As_2S_3 + 3S^{--} + 2S = 2AsS_4^{---}.$$
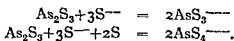
Arsenious compounds are reducing agents, $As_2O_3 + 2(O) = As_2O_5$; they reduce, e.g., cupric to cuprous compounds.

9. Dissolve the copper arsenite obtained in reaction 17 by adding dilute sodium hydroxide ; a deep blue solution is formed. Boil this, red cuprous oxide is precipitated.

The arsenious ion As^{+++} and the arsenite ion AsO_3^{---} are both colourless.

are, however, hydrolysed in aqueous solution thus, $Sb^{+++} + H_2O \rightleftharpoons SbO^+ + 2H^+$, and form insoluble oxy-salts (*e.g.*, $SbOCl$) unless sufficient strong acid is added to force the equilibrium in favour of Sb^{+++} ions.

The ionic reactions of antimony with the group reagents listed illustrate the amphoteric nature of the oxide and the ability of the orange sulphide Sb_2S_3 to form a soluble thioantimonate.

Antimony compounds when reduced on the charcoal block form antimony metal (brittle bead) with an incrustation of the oxide.

1. To a solution of antimony chloride ($SbCl_3$) in aqueous hydrochloric acid (1 ml.) add water (1 ml. at a time). A white precipitate of $SbOCl$ is formed (compare As). Add concentrated hydrochloric acid; the precipitate re-dissolves.

2. Carry out the charcoal block test with antimony oxide.

All the antimony ions considered here are colourless. The only simple salts likely to be met are the chloride and sulphide.

IONIC REACTIONS

Use antimony chloride (0·2M solution in hydrochloric acid)

No.	Reagent	Visible Result	Comments
3	**Chloride** Dil. HCl	None.	
4	**Sulphide** (a) H_2S+dil. HCl (b) H_2S+NH_4Cl +NH_4OH.	Orange ppt. Sb_2S_3. ,, ,,	Ppt. is sol. in $(NH_4)_2S_2$; formation of thioantimonate.
5	**Hydroxide** (a) NaOH . (b) NH_4OH	White ppt. $Sb(OH)_3$. ,, ,,	Sol. in excess NaOH, formation of antimonite. Insol. in excess NH_4OH.
6	**Carbonate** Na_2CO_3 or $(NH_4)_2CO_3$.	White ppt. $Sb(OH)_3$.	Carbonate does not exist.

Analytical Behaviour.

Since antimony sulphide is insoluble in water and in dilute acid, the ion is in Class A in the Cation Separation. Since the chloride is soluble (in the presence of acid) the ion is in Group 2.

MEDICAL USES

Simple antimony compounds are poisonous if taken internally. Potassium antimonyl tartrate (tartar emetic) is now little used as an emetic but is employed, together with organic antimony compounds, in the treatment of various tropical parasitic diseases.

ARSENIC COMPOUNDS

The chief compounds of pentavalent arsenic are the arsenates, *e.g.*, Na_2HAsO_4, which show many similarities to the phosphates. Arsenic acid is weak but soluble and stable ; treatment of the salts with dilute hydrochloric acid or concentrated sulphuric acid therefore causes no visible change. The arsenate ion is colourless. The alkali metal arsenates are soluble in water, all others are insoluble.

Ammonium molybdate solution forms with arsenates a complex salt similar to that formed with phosphates. The complex arsenomolybdate is precipitated only *on boiling*.

18. Carry out the molybdate reaction with sodium arsenate as for phosphate (p. 236), but boil the mixture.

IONIC REACTIONS
Use sodium arsenate (0·2M solution)

No.	Reagent	Visible Result	Comments
19	Hydrogen Dil. HCl .	None.	H_3AsO_4 is weak but stable and soluble.
20	Silver $AgNO_3$.	Buff ppt. Ag_3AsO_4.	Sol. in dil. HNO_3.
21	Barium $Ba(NO_3)_2$.	White ppt. $Ba_3(AsO_4)_2$.	Sol. in dil. HNO_3.

MEDICAL USES

Most simple arsenic compounds are poisonous if taken internally in large doses. Dilute solutions of arsenious acid or potassium arsenite are given internally in certain types of anaemia and in certain skin diseases. Arsenic compounds are also applied externally in skin affections.

The most important use of arsenic compounds in medicine is the use of organic arsenicals in the treatment of syphilis.

9, 28   **ANTIMONY**

    Valencies : 3, 5.   *Cation :* Sb^{+++}.

Antimony is very similar to arsenic,[1] but is more " metallic " in character. Its amphoteric oxide (Sb_2O_3 only is considered here) tends to act as a base more than as an acid. The salts of the cation Sb^{+++}

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[1] Antimony, like arsenic, forms a volatile hydride (SbH_3); for details see other books.

Analytical Behaviour.

Since bismuth sulphide is insoluble in water and in dilute acid, the ion is in Class A in the Cation Separation. Since the chloride is soluble (in the presence of acid) the ion is in Group 2.

MEDICAL USES

Bismuth oxynitrate and oxycarbonate are used in the treatment of various gastric complaints. Bismuth compounds are used in the treatment of syphilis.

PERIODIC GROUP VI

The " typical " and B Subgroup elements (oxygen, sulphur, etc.) are non-metals. In compounds in which they are divalent oxygen and sulphur show some resemblances, though these are often more formal than real (compare, for example, water H_2O, and hydrogen sulphide H_2S). Sulphur also shows valencies of 4 and 6 ; oxygen is quadrivalent in some organic compounds, but never sexvalent.

The A Subgroup elements (chromium, etc.) are transition metals, which resemble sulphur only in their compounds where they show the Group valency of 6 (compare chromates and sulphates). They also show several lower valencies.

9, 30   OXYGEN

Valency : 2.   *Hydrides :* H_2O, H_2O_2.   *Anion :* OH^-.

Oxygen is the foundation-stone of inorganic chemistry and its compounds, other than those with hydrogen, are considered in the sections dealing with the other elements present.

Oxygen O_2 is a colourless, odourless gas, slightly soluble in water. Oxygen forms about one-fifth by volume of the atmosphere, which may for chemical purposes be considered as oxygen, diluted with four times its own volume of nitrogen (inert in most reactions), and contaminated with a little water and carbon dioxide. Oxygen supports the combustion of many metals, many non-metals and most organic compounds more vigorously than air does. It is usually recognised by its power of rekindling a glowing splint.[1]

Oxygen may be prepared by heating potassium chlorate, manganese dioxide being added as catalyst.

$$2KClO_3 = 2KCl + 3O_2.$$

1. *Preparation.* Gas Apparatus, Type A 1. Mix potassium chlorate (1·2 g.) and manganese dioxide (0·3 g.) and spread the mixture in a thin layer along

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[1] Nitrous oxide, N_2O, which is rarely met, also supports combustion and rekindles a glowing splint, though less vigorously than oxygen. Oxygen turns alkaline pyrogallol solution brown ; nitrous oxide does not.

9, 29   BISMUTH

Valencies : 3, 5.   *Cation :* Bi^{+++}.

Bismuth resembles antimony but is more metallic in character. Its common oxide (yellow Bi$_2$O$_3$) is weakly basic and forms only a cation Bi^{+++}. This cation is readily hydrolysed by water (compare antimony, p. 241).

$$Bi^{+++} + H_2O \ \rightleftharpoons \ BiO^+ + 2H^+.$$
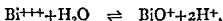
Compounds containing the group BiO are called basic salts or oxy-salts.

Bismuth compounds are reduced in the charcoal block test to metal. Since this is volatile, a yellow incrustation of oxide is also formed.

1. Dilute with water a solution of bismuth nitrate in dilute nitric acid; white bismuth oxynitrate is precipitated. Add concentrated nitric acid; the precipitate re-dissolves.

2. Carry out the charcoal block test with bismuth nitrate.

The bismuth ion Bi^{+++} is colourless.

Solubilities of Salts.

Chloride, bromide, nitrate, sulphate.	Insoluble in water, due to the formation of basic salts, which are dissolved by dilute acids.
Iodide	Insoluble in water and dilute acids.
Carbonate, phosphate	Insoluble in water, " soluble " in dilute acids.

IONIC REACTIONS

Use bismuth nitrate (0·2M solution in nitric acid)

No.	Reagent	Visible Result	Comments
3	**Chloride** Dil. HCl . .	None.	BiCl$_3$ is sol. in acid.
4	**Sulphide** (a) H$_2$S+dil. HCl . (b) H$_2$S+NH$_4$Cl +NH$_4$OH.	Dark brown ppt. Bi$_2$S$_3$. ,, ,,	Ppt. insol. in (NH$_4$)$_2$S$_2$. Bi does not form thio-salts.
5	**Hydroxide** (a) NaOH . (b) NH$_4$OH .	White ppt. Bi(OH)$_3$. ,, ,,	Insol. in excess NaOH. Insol. in excess NH$_4$OH or in NH$_4$Cl.
6	**Carbonate** Na$_2$CO$_3$ or (NH$_4$)$_2$CO$_3$.	White ppt. Bi$_2$(CO$_3$)$_3$ (basic).	
7	**Iodide** KI . .	Black ppt. BiI$_3$.	Sol. in excess KI. K[BiI$_4$] formed, orange solution.

and many reactions between these compounds are carried out in aqueous solution. All systematic inorganic qualitative analysis depends on ionic reactions carried out in aqueous solution.

Water also dissolves many organic compounds (see p. 298) and is often used as a solvent in organic reactions. Most organic compounds are, however, insoluble in water, and organic reactions are more often than not carried out in other solvents. Some organic reactions can only be carried out in the complete *absence* of water. The removal of water from solids and liquids is discussed on p. 50.

The ionisation of water, $HOH \rightleftharpoons H^+ + OH^-$, and the important subject of hydrogen and hydroxyl-ion concentration is discussed in detail in chapter 6 (pp. 91–112); some illustrative experiments are given in chapter 8 (pp. 162–168). The reactions of certain metals with water to give hydrogen, and the reactions of metallic and non-metallic oxides with water to give bases and acids, are described in the sections dealing with the other elements concerned. The hydrolysis of non-metallic halides is mentioned on p. 260.

Water forms from 70–90% of most tissues. Most cells may be considered chemically as aqueous solutions of protein, carbohydrate and mineral constituents surrounded by semi-permeable membranes.

Impurities in Water.

Distilled water which has been allowed to stand in air contains dissolved oxygen, nitrogen and carbon dioxide. The last-named forms carbonic acid, which reduces the pH of ordinary distilled water to about 5·7. The dissolved gases may be expelled by boiling the water.

Tap water contains, in addition to the impurities listed above, dissolved salts whose nature and quantity depend on the locality. The salts usually present are carbonates and sulphates of sodium, calcium and magnesium.

Salt Hydrates.

Many salts form hydrates both in solution and in the solid state, water molecules probably being linked to the metallic atoms (cations) by dative links (see p. 80). Many hydrates differ in colour from the corresponding anhydrous salts; the changes in colour attendant on the formation of the hydrates may be used as tests for water. The hydrates are usually decomposed on heating into the anhydrous salt and water, which appears as steam. (Many salts, if heated strongly, undergo further decomposition.)

8. To white anhydrous copper sulphate (1 spatula-point) add water (1 drop); the salt turns blue, owing to the formation of a hydrate $CuSO_4.5H_2O$. Heat this gently until the water is driven off; the salt becomes white again.

9. Touch anhydrous cobalt chloride paper (blue) with a wet glass rod; the paper becomes pink, due to the formation of a hydrate $CoCl_2, 6H_2O$. Place the paper on a watch-glass over a boiling water bath; the hydrate loses water and the paper becomes blue again.

the bottom of the test-tube.[1] Collect seven tubes of gas; use one tube to illustrate the sparing solubility of the gas in water and use the remaining tubes for the reactions detailed below.

2. Plunge a glowing splint into the gas; the splint is rekindled.

3. Heat charcoal (1 spatula-point) to red heat on a deflagrating-spoon in the Bunsen flame and *plunge it into the gas*. It burns, forming carbon dioxide. Test for this with lime water.

4. Heat sulphur (1 spatula-point) in a deflagrating-spoon in the Bunsen flame until it catches fire. *Plunge it into oxygen* and note that it burns much more vigorously than in air, forming sulphur dioxide. Note the smell of this; *shake it up with water (1 ml.) and show that the solution turns blue litmus red*.

5. Heat red phosphorus (1 spatula-point) and allow it to burn in oxygen. White fumes of phosphorus pentoxide are formed. Dissolve these in water (1 ml.) and test the resulting solution with litmus.

6, 7. Ignite magnesium ribbon (1 inch) and calcium (a few turnings) on a deflagrating-spoon and burn them in oxygen. Test the products with moist red litmus-paper.

The oxidation of organic compounds by oxygen is the chief source of energy for all animals. In medicine, air enriched by oxygen is administered by inspiration in cases where the normal concentration in air is insufficient.

OXIDES

These may be classified as follows :

1. *Acidic Oxides*.[2] (Most oxides of non-metals, and a few highest oxides of metals.) React with water to form acids—*e.g.* :

$$SO_2 + H_2O = H_2SO_3 \text{ (see pp. 249-250)}.$$
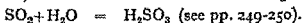
2. *Normal Basic Oxides*.[2] (Most oxides of metals.) React with water to form bases, *e.g.* :

$$MgO + H_2O = Mg(OH)_2 \text{ (see p. 196)}.$$

3. *Metallic Peroxides*. Oxides (usually of metals) which contain more oxygen than the normal oxide. Do not react with water.[3] Many give off their "extra" oxygen on heating, and oxidise *hydrochloric* acid to chlorine.

$$2PbO_2 = 2PbO + O_2$$
$$PbO_2 + 4HCl = PbCl_2 + Cl_2 + 2H_2O \text{ (see p. 225)}.$$
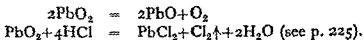
4. *Miscellaneous Oxides*. A few *neutral oxides* (water H_2O, carbon monoxide CO, nitric oxide NO) and *sub-oxides*.

WATER

Water (H_2O) is a colourless, odourless liquid (m.p.=0°; b.p.=100°; d=1·00). It is an excellent solvent for inorganic acids, bases and salts,

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[1] It will be necessary to empty the spent reaction-mixture and add fresh material to obtain seven tubes of gas.
[2] Amphoteric oxides (p. 88) have both acidic and basic character.
[3] Except sodium peroxide (see p. 189).

Hydrogen peroxide is a powerful oxidising agent,[1] yielding one atom of "oxidising oxygen" and water. $H_2O_2 = H_2O + (O)$. It oxidises iodides to iodine and lead sulphide to lead sulphate. It reacts with permanganates in acid solution, all the "available oxygen" of both substances being liberated as free oxygen (see p. 155 for use of this reaction in volumetric analysis). Hydrogen peroxide oxidises chromic acid (orange) to a blue perchromic acid soluble in organic solvents.

15, 16, 17. Examine the behaviour of hydrogen peroxide with potassium iodide solution (acidified), lead sulphide (finely-powdered), and potassium ˙˙˙˙˙˙˙˙˙˙˙˙˙˙˙˙˙˙˙˙˙˙˙˙˙ ˙˙˙˙˙˙ ichromate solution ˙˙˙˙˙˙˙˙˙˙˙˙˙˙ solution (2 drops)

9, 31   SULPHUR

Valencies : 2, 4, 6.   *Hydride* : H_2S.   *Oxides* : SO_2, SO_3.
Anions : S^{--}, sulphide ; SO_3^{--}, sulphite ;
            SO_4^{--}, sulphate ; $S_2O_3^{--}$, thiosulphate.

Sulphur is a yellow odourless solid (m.p.=115°; $d=2$) which exists in several allotropic forms. It is insoluble in and does not react with water,[3] but is soluble in carbon disulphide (*very inflammable*). It burns readily in air or oxygen with a violet flame giving sulphur dioxide.

$$S + O_2 = SO_2.$$
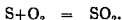
Sulphur combines with many metals (*e.g.*, iron) on heating, giving sulphides Fe+S=FeS. Sulphur combines with hydrogen at about 450°. This reaction cannot be carried out here.

1. Take sulphur (1 spatula-point) on a deflagrating-spoon, ignite it in a Bunsen flame and lower it into a boiling-tube of air. Note the smell of the gas produced, add water (1 ml.) to it and shake up. Show that the solution turns litmus red.

2. Heat in an ignition-tube sulphur and iron filings (1 spatula-point each). The mixture glows and a black solid is produced. Show that this is a sulphide (see reaction 8).

HYDROGEN SULPHIDE AND SULPHIDES

Hydrogen sulphide (sulphuretted hydrogen, H_2S) is a gas of characteristic smell, moderately soluble in water. The saturated solution in water at ordinary temperature is about 0·025M. Hydrogen sulphide is a weak dibasic[4] acid pK_a (first stage)=7·04 ; (second stage)=14·92.

---

[1] Hydrogen peroxide is used as an antiseptic; it acts as a source of "nascent oxygen."

[2] Preferable to ether, which is often used, since the latter often contains peroxides.

[3] The element sulphur is used in ointments for skin diseases.

[4] Acid salts, *e.g.* NaSH, Ba(SH)₂, are called *hydrosulphides*.

HYDROXYL ION

Bases if soluble in water give rise to hydroxyl ions OH⁻. The relationship of hydrogen and hydroxyl-ion concentrations is discussed on p. 92. Alkaline solutions—*i.e.*, solutions containing more hydroxyl than hydrogen ions—turn litmus blue. The neutralisation of a base by an acid to form a salt consists essentially in the combination of hydrogen and hydroxyl ions to form water. $H^+ + OH^- = HOH$.

Strongly alkaline solutions on standing in the air absorb carbon dioxide and become contaminated with carbonates.

$$CO_2 + 2OH^- = CO_3^{--} + H_2O.$$

The hydroxyl ion is colourless.

Solubilities of Hydroxides.

The only hydroxides soluble in water are those of sodium, potassium, ammonium, calcium and barium (the last two being only slightly soluble). All other hydroxides (and normal oxides) are insoluble in water, but " soluble " in dilute acids.

IONIC REACTIONS

Use sodium hydroxide (0·2M solution)

No.	Reagent	Visible Result	Comments
10	**Hydrogen** Dil. HCl . .	None.	OH⁻ neutralised.
11	**Silver** AgNO₃ . .	Brown ppt. Ag₂O.	Sol. in dil. HNO₃; sol. in dil. NH₄OH, due to formation of complex ion.
12	**Barium** Ba(NO₃)₂ . .	White ppt. Ba(OH)₂.	Ppt. in conc. solns. only. Sol. in dil. HNO₃.
13	**Mercuric** HgCl₂ . .	Yellow ppt. HgO.	
14	**Ammonium** NH₄Cl . .	NH₃ evolved.	Recognise by smell and behaviour to litmus.

HYDROGEN PEROXIDE

Hydrogen peroxide H_2O_2 is a liquid, which is always met as its aqueous solution (usually containing 3-30% H_2O_2). The solution is neutral.

'The sulphide ion is colourless, but many insoluble sulphides have characteristic colours. The precipitation of sulphides in varying conditions, which forms the basis of the usual method of Cation Classification, is discussed on pp. 90–91.

Solubilities of Salts.

Sodium, potassium, ammonium .	Soluble in water.
Calcium,[1] barium,[1] zinc, manganese, cobalt, nickel, ferrous.	Insoluble in water, "soluble" in dilute hydrochloric acid.
Magnesium, chromium, aluminium.	Hydrolysed by water to hydroxides.
All others	Insoluble in water and dilute hydrochloric acid.

IONIC REACTIONS

Use sodium sulphide (0·2M solution)

No.	Reagent	Visible Result	Comments
8	Hydrogen Dil. HCl .	H_2S evolved.	Acid is weak and volatile.
9	Silver $AgNO_3$.	Black ppt. Ag_2S.	Insol. in dil. HNO_3.
10	Barium $Ba(NO_3)_2$	None.	$Ba(SH)_2$ is soluble.
11	Lead $(CH_3.COO)_2Pb$ [2]	Black ppt. PbS.	Lead acetate paper may be used as a test for H_2S gas.

BIOLOGICAL RÔLE

Certain organic compounds containing divalent sulphur are of great physiological importance; some of these are treated briefly later in this book (p. 408).

SULPHUR DIOXIDE, SULPHUROUS ACID, SULPHITES

Sulphur dioxide, SO_2, is a gas of characteristic choking smell, soluble in water, giving sulphurous acid H_2SO_3. (The saturated solution is approximately 0·015M.) The gas will combine with oxygen

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[1] Hydrosulphides are soluble in water.

[2] Lead acetate. Sodium plumbite solution, Na_2PbO_2, may also be used.

Since the acid is weak and volatile it is displaced from its salts by dilute mineral acids (see reaction 8).

Hydrogen sulphide and soluble sulphides are reducing agents, being readily oxidised to sulphur.

$$H_2S+(O) = H_2O+S : \text{ or } S^{--}-2e = S.$$
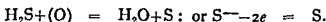
Among the oxidising agents which will carry out this oxidation are the halogens (see pp. 259 *et seq.*), oxygen (the gas burns in air with a blue flame : $2H_2S+3O_2=2H_2O+2SO_2$), nitric acid, ferric salts, dichromates and permanganates in acid solution.[1]

Some sulphides are oxidised to sulphate by hydrogen peroxide (see p. 247).

3. *Preparation.* Gas Apparatus, Type B 2. Warm gently ferrous sulphide (2 spatula-points) and dilute hydrochloric acid (5 ml.). Collect two tubes of hydrogen sulphide. Use one tube to show the solubility of the gas in water.

4. Show that hydrogen sulphide burns in air.

5. Add hydrogen sulphide water to (a) ferric chloride, (b) potassium dichromate, and (c) potassium permanganate solutions acidified with dilute sulphuric acid ; note the changes in colour—from yellow to pale green, orange to green, and violet to colourless respectively—and the formation of a precipitate or turbidity due to sulphur.

On heating alone some sulphides are oxidised, the oxide of the metal and sulphur dioxide being formed. A few sulphides sublime.

Sulphur in its divalent state is formally analogous to oxygen. Just as acidic oxides (oxides of non-metals or metalloids) and basic oxides (oxides of metals) combine to give salts—so some sulphides (those of metalloids) combine with other sulphides (usually those of alkali metals or of ammonium) to give *thio-salts*.

$$CaO+SO_3 = CaSO_4$$
$$Na_2S+SnS_2 = Na_2SnS_3 \text{ or } SnS_2+S^{--} = SnS_3^{--}.$$
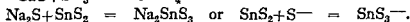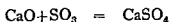
Polysulphides, corresponding to peroxides, also exist. The most important of these is yellow ammonium polysulphide, a mixture of $(NH_4)_2S_2$, $(NH_4)_2S_3$, etc., used for dissolving the sulphides of arsenic, antimony and tin.

Sulphides in alkaline solution give an intense violet colour with sodium nitroprusside $Na_2[Fe(CN)_5NO]$. The chemistry of the reaction is complicated.

6. To stannic chloride in dilute hydrochloric acid (1 ml.) add hydrogen sulphide water (5 ml.). A yellow precipitate of stannic sulphide is formed. Now add ammonium polysulphide solution ; the precipitate dissolves, with the formation of a thiostannate.

7. To sodium sulphide solution (1 ml.) add sodium nitroprusside solution (1 drop).

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[1] A white or pale yellow precipitate of sulphur formed by oxidation of hydrogen sulphide by one of the four last-mentioned reagents may be confused in qualitative analysis with a precipitate of a metallic sulphide.

Sulphuric acid H_2SO_4 is a colourless, odourless, oily liquid (b.p. (dec.)=330°; d=1.84). The usual " conc. H_2SO_4 " of the laboratory contains about 98% H_2SO_4. The acid is miscible in all proportions with water, much heat being evolved on mixing.[1] The ~~acid is dibasic, so far as the first stage in the dissociation is concerned it~~

and volatile only at about 300°, it displaces from their salts nearly all other acids (exceptions are phosphoric and silicic acids, which are still less volatile). Concentrated sulphuric acid is also a dehydrating agent and an oxidising agent[2]; it therefore dehydrates or oxidises many acids after displacing them from their salts. Details are given under the respective acids.

When acting as an oxidising agent sulphuric acid is reduced to sulphur dioxide and oxygen.

$$H_2SO_4 \;=\; H_2O+SO_2+(O).$$

Since concentrated sulphuric acid is an oxidising agent, it can " dissolve " some metals (e.g., copper, mercury) which are below hydrogen in the electro-chemical series.

Sulphuric acid being dibasic forms two series of salts; the acid salts (e.g., $KHSO_4$) give solutions which are strongly acidic.

On heating alone, sulphates (except those of the alkalis and alkaline earths, which are stable) give off sulphur dioxide and oxygen, leaving a basic oxide.

$$2CuSO_4 \;=\; 2CuO+2SO_2+O_2.$$

Sulphates on heating with charcoal are reduced to sulphides.

18. Heat copper sulphate in an ignition-tube.

19. Heat sodium sulphate (½ spatula-point) and charcoal (1 spatula-point) in an ignition-tube. Test the residue for sulphide.

Fuming sulphuric acid (oleum, $H_2S_2O_7$) is used for introducing sulphonic acid radicals into organic compounds (see pp. 319-320).

The ions SO_4^{--} and HSO_4^- are colourless.

Solubilities of Salts.

All sulphates are soluble in water except (1) those of barium and lead, insoluble in water and in dilute acids; (2) those of calcium and silver, sparingly soluble in water, and no more soluble in dilute acids; (3) a few sulphates which are hydrolysed to insoluble basic salts.

---

[1] Always add acid to water slowly with stirring, *not* water to acid.

[2] As the concentrated acid is diluted with water, these properties are steadily diminished, until in the ordinary " bench dilute H_2SO_4 " (approximately 1M) they are lost completely.

in the presence of a catalyst ; this reaction is not suitable for a students' experiment. Sulphur dioxide is a reducing agent (see below). It does *not* blacken lead acetate paper (contrast hydrogen sulphide).

Sulphurous acid (H_2SO_3) exists only in aqueous solution. On heating it decomposes into sulphur dioxide and water. It is a weak dibasic acid, pK_a (first stage)=1·77 ; (second stage)≈7·00. Since it is weak and unstable, it is displaced from its salts (sulphites) by dilute mineral acids.

The acid is a reducing agent. On oxidation it gives sulphuric acid.

$$H_2SO_3+(O) = H_2SO_4$$
$$SO_3^{--}+H_2O-2e = SO_4^{--}+2H^+.$$
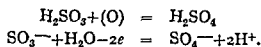
12. *Preparation of Sulphur Dioxide.* Gas Apparatus, Type B 2. Warm together sodium sulphite (4 spatula-points) and dilute hydrochloric acid (5 ml.). Collect three tubes of gas, and use one to show the solubility of the gas in water.

13. Show that sulphur dioxide does not blacken lead acetate paper but turns acid-dichromate paper green.

14. Show that sulphurous acid reduces acidified solutions of (*a*) potassium dichromate, (*b*) potassium permanganate.

The sulphite ion SO_3^{--} is colourless.

Solubilities of Salts.

Sodium, potassium, ammonium. Soluble in water.
All others   .   .   .   Insoluble in water, " soluble " in
                            dilute acids.

IONIC REACTIONS

Use sodium sulphite (0·2M solution)

No.	Reagent	Visible Result	Comments
15	**Hydrogen** Dil. HCl .	SO_2 evolved on warming.	Acid is weak and unstable.
16	**Silver** $AgNO_3$.	White ppt. Ag_2SO_3.	Sol. in dil. HNO_3.
17	**Barium** $Ba(NO_3)_2$.	White ppt. $BaSO_3$.	Sol in dil. HNO_3.

SULPHURIC ACID, SULPHATES

Sulphur trioxide SO_3, the anhydride of sulphuric acid, will not be met here.

Sulphuric acid H_2SO_4 is a colourless, odourless, oily liquid (b.p. (dec.)=$330°$; $d=1\cdot84$). The usual "conc. H_2SO_4" of the laboratory contains about 98% H_2SO_4. The acid is miscible in all proportions with water, much heat being evolved on mixing.[1] The acid is dibasic ; so far

is strong, $H_2SO_4 \rightarrow H^+ =$

is rather weak ($pK_a=$

and volatile only at about $300°$, it displaces from their salts nearly all other acids (exceptions are phosphoric and silicic acids, which are still less volatile). Concentrated sulphuric acid is also a dehydrating agent and an oxidising agent[2] ; it therefore dehydrates or oxidises many acids after displacing them from their salts. Details are given under the respective acids.

When acting as an oxidising agent sulphuric acid is reduced to sulphur dioxide and oxygen.

$$H_2SO_4 \ = \ H_2O + SO_2 + (O).$$

Since concentrated sulphuric acid is an oxidising agent, it can "dissolve" some metals (e.g., copper, mercury) which are below hydrogen in the electro-chemical series.

Sulphuric acid being dibasic forms two series of salts ; the acid salts (e.g., $KHSO_4$) give solutions which are strongly acidic.

On heating alone, sulphates (except those of the alkalis and alkaline earths, which are stable) give off sulphur dioxide and oxygen, leaving a basic oxide.

$$2CuSO_4 \ = \ 2CuO + 2SO_2 + O_2.$$

Sulphates on heating with charcoal are reduced to sulphides.

18. Heat copper sulphate in an ignition-tube.

19. Heat sodium sulphate ($\frac{1}{2}$ spatula-point) and charcoal (1 spatula-point) in an ignition-tube. Test the residue for sulphide.

Fuming sulphuric acid (oleum, $H_2S_2O_7$) is used for introducing sulphonic acid radicals into organic compounds (see pp. 319-320).

The ions SO_4^{--} and HSO_4^- are colourless.

Solubilities of Salts.

All sulphates are solil   ept (?) those of l

few sulphates which are hydr

dim

IM) they are lost completely.

IONIC REACTIONS

Use sodium sulphate (0·2M solution)

No.	Reagent	Visible Result	Comments
20	Hydrogen Dil. HCl . .	None.	H_2SO_4 is strong and stable.
21	Silver AgNO₃ . .	None.	Ag_2SO_4 is soluble.
22	Barium Ba(NO₃)₂ .	White ppt. $BaSO_4$.	Insol. in dil. HNO_3.
23	Lead (CH₃ COO)₂Pb .	White ppt. $PbSO_4$.	Insol. in dil. HNO_3.
24	Calcium CaCl₂ . .	White ppt. $CaSO_4$.	Ppt. formed in conc. solns. only. $CaSO_4$ is slightly soluble.

BIOLOGICAL RÔLE AND MEDICAL USES

The sulphate ion is present in human plasma in very small amounts. Its rôle is not known. Many undesirable organic hydroxy compounds are converted in the body into their sulphuric acid esters (see p. 429) which are probably less active physiologically and, being water-soluble, are excreted in the urine.

Since sulphate is a foreign ion in the human body not much absorbed in the intestine, sulphates raise the osmotic pressure of the intestinal contents; they attract water from the surrounding tissues and the bulk of fluid so produced in the intestine exerts a purgative action (hence the use of sodium and magnesium sulphates, Glauber's and Epsom salts).

THIOSULPHATES

The principal importance of thiosulphates in the laboratory lies in the use of sodium thiosulphate, $Na_2S_2O_3$, as a reducing agent for the determination of iodine (see pp. 115 and 156). In this reaction the thiosulphate ion is oxidised to the tetrathionate ion $S_4O_6^{--}$ (which is otherwise of no importance).

$$2S_2O_3^{--} = S_4O_6^{--} + 2e.$$

25. Add sodium thiosulphate solution to a dilute solution of iodine in potassium iodide.

The salts are called "thiosulphates" because they may be looked upon as sulphates in which one atom of oxygen has been replaced by one atom of divalent sulphur (compare the thioarsenates and other thio-salts referred to under sulphides; also thiocyanates).

The acid $H_2S_2O_3$ is weak and unstable, breaking down on formation to give sulphur dioxide, sulphur and water.

$$H_2S_2O_3 = H_2O + SO_2 + S. \quad \text{(See reaction 26.)}$$
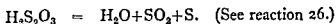
The ion $S_2O_3^{--}$ is colourless.

Solubilities of Salts.

Sodium, potassium, ammonium, calcium and barium.	Soluble in water.
All others . . .	Insoluble in water—many "dissolve" in alkali thiosulphate solutions to give complex compounds.

IONIC REACTIONS

Use sodium thiosulphate (0·2M solution)

No.	Reagent	Visible Result	Comments
26	Hydrogen Dil. HCl .	Yellow ppt. S; SO_2 evolved.	Acid is weak and unstable.
27	Silver $AgNO_3$.	White ppt. $Ag_2S_2O_3$.	Sol. in excess $Na_2S_2O_3$, giving $Na_3[Ag(S_2O_3)_2]$. Dec. on standing, giving black Ag_2S.
28	Barium $Ba(NO_3)_2$.	White ppt. BaS_2O_3.	In conc. solns. only. BaS_2O_3 is slightly sol.

OTHER SULPHUR COMPOUNDS

The *halides* of sulphur are not important. The *oxy-halides*, thionyl chloride $SOCl_2$, sulphuryl chloride SO_2Cl_2, and chlorosulphonic acid $ClSO_3H$, are much used for the introduction of chlorine and of sulphur-containing radicals into organic compounds (compare phosphorus pentachloride).

Sodium hydrosulphite, $Na_2S_2O_4$, a powerful reducing agent, will be met in the reactions of haemoglobin (pp. 412-413).

9, 3²   CHROMIUM

> *Valencies :* 3, 6.
> *Oxides :* Cr_2O_3, CrO_3.
> *Cation :* Cr^{+++}.
> *Anions :* CrO_4^{--}, chromate ; $Cr_2O_7^{--}$, dichromate.

CHROMATES AND DICHROMATES

The most important compounds of chromium [1] are those derived from the acidic oxide [2] CrO_3, in which the element shows its group valency of 6. These compounds, the chromates (CrO_4^{--} ion, yellow) and dichromates ($Cr_2O_7^{--}$ ion, orange-red) are powerful oxidising agents. Their reduction products are chromic salts (Cr^{+++} ion, green) derived from the oxide Cr_2O_3. The half-equation for the reduction of a dichromate in acid solution is

$$Cr_2O_7^{--} + 14H^+ + 6e = 2Cr^{+++} + 7H_2O,$$
$$2CrO_3 = Cr_2O_3 + 3(O).$$
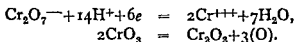
Dichromates are widely used as oxidising agents, both in inorganic and organic [3] chemistry. Some inorganic compounds oxidised by dichromates are iodides, sulphites (or sulphur dioxide), sulphides (or hydrogen sulphide), ferrous salts, stannous salts.

1. To potassium dichromate solution acidified with dilute sulphuric acid, add (*a*) sulphurous acid, (*b*) hydrogen sulphide solution. Note the colour change from orange to green.

The ions CrO_4^{--} and $Cr_2O_7^{--}$ are easily interconvertible in solution ; chromates on acidification give dichromates ; the latter on the addition of alkali give chromates.

$$2CrO_4^{--} + 2H^+ = Cr_2O_7^{--} + H_2O \quad \text{(yellow to red)}.$$
$$Cr_2O_7^{--} + 2OH^- = 2CrO_4^{--} + H_2O \quad \text{(red to yellow)}.$$
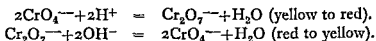
Dilute hydrochloric acid transforms chromates to dichromates but does not react further with the latter. Concentrated sulphuric acid liberates the acid anhydride CrO_3. " Chromic acid cleaning mixture," made by dissolving sodium dichromate (2 g.) in water (5 ml.) and adding concentrated sulphuric acid (65 ml.), is a solution of chromium trioxide in sulphuric acid ; *the chromium trioxide oxidises organic matter adhering to dirty glassware, and the sulphuric acid dissolves the decomposition products.*

Dichromates in acid solution react with peroxides to give an unstable blue perchromic acid ($HCrO_5$?) soluble in organic solvents (see p. 247).

Solubilities of Salts.

Sodium, potassium, ammonium,   Soluble in water.
    calcium, magnesium.
All others   .   .   .   .   Insoluble in water, " soluble " in
                                  dilute acids.

IONIC REACTIONS OF CHROMATES
Use potassium chromate (0·1M solution)

No.	Reagent	Visible Result	Comments
2	Hydrogen Dil. HCl .	Yellow soln. becomes red.	Dichromate formed.
3	Silver AgNO₃ .	Red-brown ppt. Ag_2CrO_4.	Sol. in dil. HNO_3.
4	Barium Ba(NO₃)₂ .	Yellow ppt. $BaCrO_4$.	Sol. in dil. HNO_3.

IONIC REACTIONS OF DICHROMATES
Use potassium dichromate (0·1M solution)

No.	Reagent	Visible Result	Comments
5	Hydrogen Dil. HCl .	None.	
6	Silver AgNO₃ .	Red-brown ppt. $Ag_2Cr_2O_7$.	Sol. in dil. HNO_3.
7	Barium Ba(NO₃)₂ .	Yellow ppt. $BaCr_2O_7$.	Sol. in dil. HNO_3.
8	Hydroxide NaOH .	Red solution becomes *yellow*.	Chromate formed.

CHROMIC SALTS

Chromic salts (Cr^{+++} ion) are derived from the green oxide Cr_2O_3. The hydroxide, $Cr(OH)_3$, is amphoteric, and the chromite (green solution) obtained by dissolving $Cr(OH)_3$ in excess sodium hydroxide

may be oxidised by hydrogen peroxide to a chromate. The oxide is not reduced by carbon; it is therefore left as a residue when chromium compounds are heated on the charcoal block. Chromium forms a green borate in the borax bead test (both oxidising and reducing flames).

9. Treat the chromite solution obtained in reaction 14 (a) with hydrogen peroxide.

10, 11. Use chromium sulphate for the charcoal block and borax bead tests.

The chromic ion is green.

Trivalent chromium forms many complex ions with water, ammonia and anions.

Solubilities of Salts.

Halides, sulphate and nitrate . . Soluble in water.
Sulphide and carbonate . . Hydrolysed to the insoluble hydroxide.

IONIC REACTIONS

Use chromium sulphate (o·2M solution)

No.	Reagent	Visible Result	Comments
12	**Chloride** Dil. HCl . .	None.	$CrCl_3$ is sol.
13	**Sulphide** (a) H_2S+dil. HCl.	None.	Cr_2S_3 is hydrolysed by water.
	(b) H_2S+NH_4Cl $+NH_4OH.$	Green ppt. $Cr(OH)_3$. —	
14	**Hydroxide** (a) NaOH . .	Green ppt. $Cr(OH)_3$.	Sol. in excess NaOH, giving chromite.
	(b) NH_4OH . .	,, ,,	Insol. in excess NH_4OH or in NH_4Cl.
15	**Carbonate** Na_2CO_3 or $(NH_4)_2CO_3$.	Green ppt. $Cr(OH)_3$.	$Cr_2(CO_3)_3$ does not exist.

Analytical Behaviour.

Since chromium sulphide is hydrolysed to the hydroxide, chromium is not precipitated in Class A (Groups 1 and 2). The hydroxide is precipitated by ammonium hydroxide and ammonium chloride, and the metal is therefore in Class B, Group 3.

PERIODIC GROUP VII

The " typical " and B Subgroup elements (the *halogens*, fluorine, chlorine, bromine, iodine) are non-metals ; they show a marked family resemblance, but the electronegative character decreases steadily from fluorine to iodine. All show the Group valency of 1 in their most important compounds ; chlorine and iodine show the Group valency of 7 ; intermediate valencies of 3 and 5 are also found. Fluorine shows many differences from the other three halogens both, in its inorganic and its organic compounds.

The A Subgroup elements (manganese, etc.) are transition metals, whose only resemblance to the halogens is in the compounds where the elements display their Group valency of 7 (compare permanganates and perchlorates). They also show several lower valencies.

9, 33   FLUORINE

Valency : 1.   *Hydride* : HF.   *Anion* : F⁻.

Fluorine F_2, a pale greenish-yellow gas, which is the most reactive element known, will not be met in the laboratory.

HYDROFLUORIC ACID, FLUORIDES

Hydrogen fluoride HF is a colourless gas, whose solution in water is a strong acid, hydrofluoric acid. This acid attacks silica and glass, forming silicon tetrafluoride SiF_4 ; it is therefore kept in platinum or guttapercha bottles.

Since the acid is strong, it is *not* displaced from its salts by dilute hydrochloric acid ; since it is volatile and stable, concentrated sulphuric acid displaces the acid from its salts, but does not transform it further.

$$NaF + H_2SO_4 \;=\; HF\!\uparrow + NaHSO_4.$$

The acid acts on silica, giving the volatile silicon tetrafluoride which reacts with water to re-form hydrofluoric acid and silica.

$$SiO_2 + 4HF \;=\; SiF_4\!\uparrow + 2H_2O.$$
$$SiF_4 + 2H_2O \;=\; SiO_2\!\downarrow + 4HF.$$
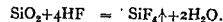
1. Treat sodium fluoride with concentrated sulphuric acid.

2. Mix sodium fluoride (1 spatula-point) and silica (a speck) in a small nickel crucible and add con   .   .   .   .   .
are evolved ; if a drop of water (.   .   :   .
cloudy by silica, produced by hydr   .   .   .   .

The fluoride ion is colourless.

R

Solubilities of Salts.

Sodium, potassium, ammonium, silver,   Soluble in water.
  mercuric.
All others .   .   .   .   . Insoluble in water.

Contrast the solubilities of the other halides.

IONIC REACTIONS
Use potassium fluoride (0·2M solution)

No.	Reagent	Visible Result	Comments
3	Hydrogen Dil. HCl . .	None.	Acid is strong and stable.
4	Silver AgNO₃ . .	None.	AgF is sol.
5	Barium Ba(NO₃)₂ . .	White ppt. BaF₂.	Sparingly sol. in dil. HNO₃.

BIOLOGICAL RÔLE
Fluorides are concerned in the formation of dental enamel.

9, 34　　　　　　　　　　CHLORINE

Valencies : 1, 3, 5, 7.　　*Oxides :* Cl_2O, ClO_2.　　*Hydride :* HCl.
Anions : Cl^-, chloride ; ClO^-, hypochlorite ; ClO_3^-, chlorate ;
ClO_4^-, perchlorate.

Chlorine Cl_2 is a dense greenish-yellow gas of characteristic smell. It is moderately soluble in water ; the solution, " chlorine water," decomposes [1] slowly on keeping thus :

$$Cl_2 + H_2O = HCl + HClO ; 2HClO = 2HCl + O_2\uparrow.$$
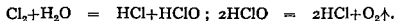
Chlorine does not combine with oxygen, but combines with hydrogen and with phosphorus (not suitable for students' experiments). It combines with many metals, either in the cold or on heating, forming chlorides.

Chlorine may be prepared by the oxidation of hydrochloric acid with potassium permanganate.

$$2KMnO_4 + 16HCl = 2KCl + 2MnCl_2 + 8H_2O + 5Cl_2.$$

---

[1] Chlorine water in reagent bottles does not keep indefinitely. Make sure that the reagent smells strongly of chlorine before using it.

Prob----- · · C'·· · .·.   Add concentrated
                                        Collect three tubes
                                        comparison and the

~turbidity test.~

2. Heat iron filings (1 spatula-point) in a deflagrating-spoon and plunge them into a tube of chlorine. The iron burns, forming ferric chloride (brown fumes). Shake with water and show that the solution gives the reactions of ferric ion (p. 272).

Chlorine is strongly electronegative and displaces bromine, iodine and sulphur from bromides, iodides and sulphides. This is an oxidation, *e.g.*,

$$\begin{aligned} Cl_2 + 2e &= 2Cl^- \\ 2I^- &= I_2 + 2e \\ \hline Cl_2 + 2I^- &= I_2 + 2Cl^-. \end{aligned}$$
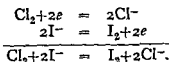
Chlorine acts as an oxidising agent in other reactions, *e.g.*, oxidation of ferrous to ferric salts, oxidation of sulphurous to sulphuric acid. The bleaching action of moist chlorine (*e.g.*, on moist litmus-paper) is due to its oxidising powers. Chlorine reacts with cold dilute caustic alkalis to give chloride and hypochlorite ions.

$$Cl_2 + 2OH^- = Cl^- + ClO^- + H_2O.$$
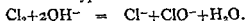
3. Treat the following with chlorine water: (*a*) potassium iodide solution, (*b*) starch iodide paper, (*c*) sodium sulphide solution, (*d*) ferrous sulphate solution, (*e*) sulphurous acid, (*f*) sodium hydroxide solution.

MEDICAL USES

Chlorine is a powerful antiseptic. Many compounds which slowly give rise to chlorine are used for this purpose, *e.g.*, hypochlorites (bleaching powder or sodium h~----~ · ·   ·   ·.·.
(an organic com

HYDROCHLORIC ACID, CHLORIDES

Hydrogen chloride (HCl) is a colourless gas, slightly denser than air, which " fumes " in moist air (the fumes are due to condensation with moisture); it is extremely soluble in water, giving a solution which is a strong acid. The term " hydrochloric acid " should be applied to this solution, and not to the gas. The " conc. HCl " of the laboratory is an aqueous solution containing about one-third its weight of HCl.

Hydrochloric acid is displaced from its salts by concentrated sulphuric acid, not because the latter is stronger, but because it is non-volatile.

$$\begin{aligned} NaCl + H_2SO_4 &= NaHSO_4 + HCl\uparrow \text{ (cold).} \\ NaHSO_4 + NaCl &= Na_2SO_4 + HCl\uparrow \text{ (hot).} \end{aligned}$$
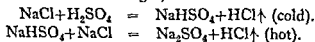
The acid and the chloride ion are oxidised to chlorine by peroxides, permanganates, etc.

$$\begin{aligned} 2Cl^- - 2e &= Cl_2, \\ \text{or} \qquad 2HCl + (O) &= Cl_2 + H_2O. \end{aligned}$$
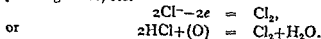
4. *Preparation of Hydrogen Chloride.* Gas Apparatus, Type B 2. Add concentrated sulphuric acid (5 ml.) to sodium chloride (3 g.). Collect four tubes of gas. Use two tubes for density comparison and one tube to show the

. . . . when a glass rod, moistened with concentrated ammonia, is brought near the mouth of a tube of hydrogen chloride.

7. Heat dilute hydrochloric acid with manganese dioxide (MnO_2).
8. Treat dilute hydrochloric acid with potassium permanganate ($KMnO_4$, ¼ spatula-point), without heating.

Most *metallic* chlorides are *solids* which are *electrolytes*, giving in aqueous solution the chloride ion Cl^-. Most of them are stable to heat ; a few (*e.g.*, mercuric chloride) sublime.

Most *non-metallic* chlorides are *liquids*, which are *non-electrolytes*, and are decomposed by water, thus, *e.g.*, phosphorus pentachloride.

$$PCl_5 + 4HOH = H_3PO_4 + 5HCl.$$

9. Add water (1 drop) to phosphorus pentachloride (¼ spatula-point). Fumes of hydrochloric acid are evolved.

The chloride ion Cl^- is colourless.

Solubilities of Salts.

All are soluble in water except the following : (*a*) silver, mercurous and lead chlorides (the last named is sparingly soluble in cold water, considerably more soluble in hot water) ; these three chlorides are no more soluble in dilute acids than they are in water, *and* (*b*) some chlorides, *e.g.*, that of bismuth, which are hydrolysed by water to give insoluble basic salts or oxides ; these salts will dissolve in the presence of dilute hydrochloric acid or of any other dilute strong acid.

IONIC REACTIONS

Use sodium chloride (0·2M solution)

No.	Reagent	Visible Result	Comments
10	Hydrogen Dil. HCl . .	None.	
11	Silver $AgNO_3$ . .	White ppt. AgCl.	Insol. in dil. HNO_3, sol. in dil. NH_4OH due to formation of complex ion.
12	Barium $Ba(NO_3)_2$ . .	None.	$BaCl_2$ is sol.
13	Lead $Pb(OOC.CH_3)_2$ * . .	White ppt. $PbCl_2$.	Ppt. in conc. solns. only.

* Acetate.

BIOLOGICAL RÔLE AND MEDICAL USES

The chloride ion is quantitatively the most important inorganic anion. It is present in human plasma (usually about 360 mg. per 100 ml.). It passes very readily through the membranes of the red blood cells, and plays an important part in maintaining osmotic and electrical equilibrium between the plasma and the red cell contents. Hydrochloric acid is the strong acid present in gastric contents (about 0·2 %).

A 0·9% sodium chloride solution, "normal saline," is isotonic with human plasma and is injected intravenously to restore lost body fluids or as a vehicle for drugs. A similar solution containing a trace of potassium and calcium chlorides (Ringer's solution) is used for the same purposes. Hydrochloric acid is sometimes administered when the concentration in the stomach is abnormally low.

HYPOCHLORITES

Hypochlorites … the … … … … …

chlorine slowly, so the salts and their solutions always smell of this.

$$OCl^- + 2H^+ + Cl^- = Cl_2 + H_2O.$$
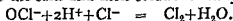
Hypochlorite solutions turn litmus blue, then bleach it.

Cobalt salts *catalyse* the decomposition of hypochlorite ions into chloride ions and oxygen.

$$2ClO^- = 2Cl^- + O_2\uparrow.$$
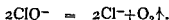
14. Treat bleaching powder … … … … … …
15. "
(1 dro
is evolved (test with glowing splint).

Hypochlorites are always contaminated with chlorides, which will be recognised by precipitation with silver nitrate.

CHLORATES

Chlorates ($KClO_3$) are important as oxidising agents.[1] Chloric acid ($HClO_3$) is unstable, decomposing on warming to give the highly explosive chlorine dioxide ClO_2, a yellow gas.

Chlorates show no visible change with cold dilute hydrochloric acid, but on warming, chlorine dioxide and chlorine are evolved. Chlorates react violently with concentrated sulphuric acid, forming chlorine dioxide. Chlorates on heating evolve oxygen (see preparation of the latter, pp. 243–244).

16. Warm potassium chlorate ($\frac{1}{2}$ spatula-point) with dilute hydrochloric acid.
17. *Care.* To potassium chlorate ($\frac{1}{6}$ spatula-point) add concentrated sulphuric acid (3 drops) and heat cautiously.

The chlorate ion ClO_3^- is colourless. All chlorates are soluble in water. The ion cannot therefore be detected by precipitation reactions.

---

[1] They are sometimes used as germicides.

PERCHLORATES

Perchloric acid ($HClO_4$) is used as a reagent for potassium (see p. 191). Perchlorates are important theoretically as the only chlorine compounds for which manganese analogues (the permanganates) are known.

9, 35   BROMINE

Valencies: 1, 3, 5.   *Hydride:* HBr.

Anions: Br⁻, bromide ; BrO⁻, hypobromite ; BrO_3^-, bromate.

Bromine is a dense volatile reddish-brown liquid (b.p.=59°; d=3·2), which gives a choking reddish-brown vapour (*poisonous*). *All work with free bromine should be done in a fume cupboard and care should be taken not to inhale the vapour or to let the liquid touch the skin.*

The chemistry of bromine and its compounds closely resembles that of chlorine and its compounds. The most important differences are (1) bromine is less strongly electronegative than chlorine, (2) hydrobromic acid and bromides are more easily oxidised to bromine than are the corresponding chlorine compounds to chlorine.

The combination of bromine with hydrogen is not suitable for a students' experiment. Bromine reacts with phosphorus, forming phosphorus tribromide.

$$2P+3Br_2 = 2PBr_3.$$

The latter is hydrolysed by water to phosphorous and hydrobromic acids.

$$PBr_3+3HOH = H_3PO_3+3HBr.$$
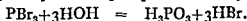
1. To moist red phosphorus (1 spatula-point) add bromine (1 drop). There is a flash as the bromine strikes the phosphorus. Subsequently white fumes of hydrobromic acid are evolved.

Bromine is more soluble in carbon tetrachloride CCl_4, or chloroform $CHCl_3$, than in water. It is extracted from water by these solvents, giving a brown solution.

Bromine is an oxidising agent, displacing iodine and sulphur from their salts (compare chlorine).

$$Br_2+2e = 2Br^-.$$

Bromine reacts with dilute caustic alkalis as chlorine does, giving bromide and hypobromite.

$$Br_2+2OH^- = Br^-+BrO^-+H_2O.$$

2. Add bromine water (5 drops) to solutions of (a) potassium iodide, (b) sodium sulphide, and (c) sodium hydroxide. Note that in the last two cases the colour of the bromine is discharged.

HYDROBROMIC ACID, BROMIDES

Hydrogen bromide gas (HBr) and its solution in water, hydrobromic acid, are very similar to hydrogen chlorine and its solution. Hydro-

bromic acid is a *strong* acid ; it is therefore *not* displaced from its salts by any other acids in conditions of fair competition (see reaction 5 below). It is, however, displaced from its salts by concentrated sulphuric acid (since it is volatile and the latter is not), and when liberated is partly oxidised by the sulphuric acid to bromine.

$$2HBr+(O) = Br_2+H_2O.$$

Hydrobromic acid is slowly oxidised by atmospheric oxygen ; its solutions slowly turn brown on standing. The acid and its salts are also oxidised by chlorine and by permanganates in acid solution.

3. *Heat sodium bromide with concentrated sulphuric acid.*

4. Add to sodium bromide solution (1 ml.) carbon tetrachloride (1 ml.) followed by chlorine water (2 drops), and shake. The lower (carbon tetrachloride) layer is coloured brown by bromine.

The bromide ion Br⁻ is colourless.

Solubilities of Salts.

These are exactly similar to those of the chlorides ; silver and mercurous bromides are insoluble in water and dilute acids ; lead bromide is sparingly soluble in cold water, more soluble in hot water ; some bromides are hydrolysed to insoluble basic salts.

IONIC REACTIONS

Use sodium bromide (0·2M solution)

No.	Reagent	Visible Result	Comments
5	Hydrogen Dil. HCl . .	None.	Acid is strong and stable.
6	Silver AgNO₃ . .	Cream ppt. AgBr.	Insol. in dil. HNO₃, sparingly sol. in dil. NH₄OH.
7	Barium Ba(NO₃)₂ . .	None	BaBr₂ is sol.
8	Lead (CH₃.COO)₂Pb .	White ppt. PbBr₂.	In conc. solns. only. PbBr₂ is sparingly sol.

MEDICAL USES

Bromides (of sodium, potassium and ammonium) are used in medicine as sedatives.

OTHER BROMINE COMPOUNDS

The bromides of *non-metals* (*e.g.*, phosphorus tribromide, PBr$_3$) are non-electrolytes which are hydrolysed by water (compare non-metallic chlorides and see reaction 1 above).

Hypobromites (*e.g.*, NaBrO) are used as oxidising agents (see reaction with p. 425).

Bromates (*e.g.*, NaBrO$_3$) are used as standards in oxidation-reduction titrations (see p. 157).

9, 36   IODINE

Valencies: 1, 3, 5, 7.   *Hydride*: HI.

Anions: I$^-$, iodide; IO$^-$, hypoiodite; IO$_3^-$, iodate.

The chemistry of iodine and its compounds closely resembles that of chlorine and bromine and their compounds. Iodine is *less* electro-negative than either chlorine or bromine, and hydriodic acid and iodides are more easily oxidised than the corresponding chlorine and bromine compounds.

Iodine I$_2$ is a black crystalline solid, which on heating sublimes, giving a violet vapour. It is very sparingly soluble in water, but readily soluble in solutions of iodides (*e.g.*, potassium iodide), giving brown solutions containing I$_3^-$ ions. Iodine gives, with starch solution, a *blue* colour due to the formation of an adsorption compound. The blue starch-iodine colour is much deeper than the yellow or brown colour of a solution of iodine of the same concentration in aqueous iodide. Starch solution is therefore used to test for free iodine.

Iodine is more soluble in hydrocarbons or organic halogen com-pounds (*e.g.*, carbon tetrachloride CCl$_4$) than in aqueous iodide solutions, and is therefore extracted by the former solvents. Solutions of iodine in hydrocarbons or organic halogen compounds are *red* or *violet*; solutions of iodine in organic compounds containing oxygen or nitrogen are *brown*.

Iodine is a weak oxidising agent (used generally in aqueous potassium iodide solution). When reduced it gives colourless iodide ions.
I$_2$+2e=2I$^-$.

Iodine oxidises hydrogen sulphide to sulphur, and thiosulphate ions (S$_2$O$_3^{--}$) to tetrathionate ions (S$_4$O$_6^{--}$). The latter reaction is much used for the volumetric determination of iodine, and of oxidising
$$\begin{array}{r} \text{5-158).} \\ \text{(IO}^-\text{)} \\ +\text{H}_2\text{O.} \end{array}$$
Iodine solutions are therefore decolorised by the addition of sodium or potassium hydroxide (see iodoform reaction in organic chemistry, p. 335).

1. Test the solubility of iodine ($\frac{1}{2}$ spatula-point) in water, potassium iodide solution, carbon tetrachloride (1 ml. each).

2. To starch solution (1 ml.) add a solution of iodine in aqueous potassium iodide (1 drop). Note the deep blue colour.

3. Shake together iodine in aqueous potassium iodide (1 ml.) and carbon tetrachloride (1 ml.). The iodine is almost completely extracted by the carbon tetrachloride.

4. Add iodine in aqueous potassium iodide to solutions of (a) hydrogen sulphide, (b) sodium thiosulphate, (c) sodium hydroxide.

HYDRIODIC ACID, IODIDES

Hydrogen iodide and its aqueous solution, hydriodic acid, resemble hydrogen chloride and hydrochloric acid closely, except that HI is much more easily decomposed by heat and much more easily oxidised than HCl. Hydrogen iodide is a gas, extremely soluble in water. H......... . . . .   .   . : .   .re not displaced from its

.   .   .   . its salts by concentrated

.   .   .   . oxidised to iodine.

Iodide ions in acidic or neutral solutions are readily oxidised to free iodine. $2I^- - 2e = I_2$. Hydrogen iodide is also readily oxidised to iodine. $2HI + (O) = I_2 + H_2O$.

The reagents which oxidise iodide ions thus include chlorine [1] and bromine (neutral or acid), cupric salts, bromates and iodates (acid), permanganates and dichromates (acid). (For details of reactions see pp. 156-158, which dealt with the volumetric determination of these oxidising agents by means of iodide and thiosulphate solutions.)

5. (a) Treat solid potassium iodide with concentrated sulphuric acid.

(b) To potassium iodide solution (1 ml.) add carbon tetrachloride (1 ml.), followed by chlorine water (2 drops), and shake. The lower (carbon tetrachloride) layer is coloured violet.

(c) To potassium iodide solution (1 ml.) add starch solution (2 drops), followed by chlorine water (2 drops). The solution becomes deep blue.

(d) Treat potassium iodide solution (1 ml.) with dilute sulphuric acid (2 ml.) and potassium permanganate solution (5 drops). Shake with carbon tetrachloride.

The iodide ion I⁻ is colourless.

Solubilities of Salts.

Silver, mercurous, mercuric, bismuth, stannous.	Insoluble in water and in dilute acids.
Lead	Sparingly soluble in cold water, moderately soluble in hot water.
Ferric, cupric . . .	Do not exist.
All others	Soluble in water.

[1] If excess chlorine is used, it may react with iodine to form iodine mono-chloride (ICl, pale yellow), or may oxidise the iodine to iodate (IO_3^- ion, colourless).

IONIC REACTIONS

Use potassium iodide (0·1M solution)

No.	Reagent	Visible Result	Comments
6	**Hydrogen** Dil. HCl . .	None.	HI is strong and stable in these conditions.
7	**Silver** AgNO₃ soln. .	Pale yellow ppt. AgI.	Insol in dil. HNO₃. Insol. in dil. NH₄OH.
8	**Barium** Ba(NO₃)₂ soln. .	None.	BaI₂ is sol.
9	**Lead** Lead acetate soln. .	Golden-yellow ppt. PbI₂.	Test more sensitive for I⁻ than for Cl⁻ or Br⁻. Ppt. sol. in much boiling water; crystallises as golden spangles on cooling.
10	**Mercuric** HgCl₂ soln. .	Ppt. at first yellow, then pink, finally red, HgI₂.	See reactions of mercuric ion, p. 206.

OTHER IODINE COMPOUNDS

Non-metal iodides, apart from hydrogen iodide, are unimportant.

Hypoiodites (*e.g.*, NaIO) will be met as mild oxidising agents in organic chemistry (iodoform reaction, p. 335).

Iodates (*e.g.*, KIO₃) are used as standards in oxidation-reduction titrations (see p. 156). Potassium bi-iodate (KIO₃.HIO₃), being a stable solid acid salt, is useful as a primary standard in acid-base titrations (see pp. 142-143).

BIOLOGICAL RÔLE AND MEDICAL USES

A most important naturally-occurring iodine compound is the amino-acid thyroxine, the hormone of the thyroid gland.

Iodine is used in aqueous alcoholic solution as an external antiseptic (tincture of iodine). It is poisonous if taken internally. Iodine, having a high atomic weight, is opaque to X-rays, and certain organic iodine compounds are used for rendering internal organs visible under X-rays.

9, 37   MANGANESE

Valencies : 2, 4, 7.   *Cation :* Mn^{++}.
Oxides : MnO, MnO_2, Mn_2O_7.   *Anion :* MnO_4^-.

The chemistry of manganese resembles in general that of chromium.
The highest oxide (Mn_2O_7), in which the element shows its Group
valency (7), is *acidic*, and the salts formed from this oxide (perman-
ganates, *e.g.,* $KMnO_4$) are important oxidising agents. The lowest
oxide (MnO) is basic and its derivatives (manganous salts, *e.g.,* $MnSO_4$)
are reduction products of permanganates. An intermediate oxide
(MnO_2) is stable, and is the only oxide likely to be met.

PERMANGANATES

T⸱⸱ ⸱ ⸱⸱ ⸱⸱ ⸱   ⸱ ⸱ ⸱ ⸱   permanganates (MnO_4^- ion) are
⸱ ⸱ ⸱ ⸱   ⸱ ⸱   ⸱   ⸱ :   their deep violet colour, both in
⸱ ⸱ ⸱   ⸱⸱ ⸱ ⸱ ⸱ , the MnO_4^- ion is violet). They
are derived from the acid $HMnO_4$, the anhydride of which is the oxide
Mn_2O_7; both of these are dangerously unstable, and of no practical
importance.

When permanganates act as oxidising agents in *acid* solution [2] they
are reduced to manganous salts (Mn^{++} ion, very pale pink, almost
colourless).

$$MnO_4^- + 8H^+ + 5e = Mn^{++} + 4H_2O$$
$$2KMnO_4 = K_2O + 2MnO_2 + 5(O).$$

An acidified solution of a permanganate oxidises the following,
being itself reduced as shown above, and decolorised :

(a) chlorides, bromides, iodides and the corresponding acids to
    chlorine, bromine, iodine ;

(b) sulphides to sulphur ;

(c) sulphites to sulphates (SO_3^{--} to SO_4^{--}) ;

(d) nitrites to nitrates (NO_2^- to NO_3^-) ;

(e) ferrous to ferric salts (Fe^{++} to Fe^{+++}) ;

(f) stannous to stannic salts (Sn^{++} to Sn^{++++}) ;

(g) hydrogen peroxide ; all the available oxygen of both sub-
    stances is liberated.

---

[1] Potassium and sodium permanganates are used as disinfectants ; the
compounds presumably owe the value to the available oxygen present.
[2] For the use of potassium permanganate in volumetric analysis see pp.
153-155.

IONIC REACTIONS

Use potassium iodide (0·1M solution)

No.	Reagent	Visible Result	Comments
6	**Hydrogen** Dil. HCl .	None.	HI is strong and stable in these conditions.
7	**Silver** AgNO₃ soln. .	Pale yellow ppt. AgI.	Insol in dil. HNO₃. Insol. in dil. NH₄OH.
8	**Barium** Ba(NO₃)₂ soln. .	None.	BaI₂ is sol.
9	**Lead** Lead acetate soln. .	Golden-yellow ppt. PbI₂.	Test more sensitive for I⁻ than for Cl⁻ or Br⁻. Ppt. sol. in much boiling water; crystallises as golden spangles on cooling.
10	**Mercuric** HgCl₂ soln. . .	Ppt. at first yellow, then pink, finally red, HgI₂.	See reactions of mercuric ion, p. 206.

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9, 37   MANGANESE

Valencies : 2, 4, 7.   *Cation :* Mn++.
Oxides : MnO, MnO₂, Mn₂O₇.   *Anion :* MnO₄⁻.

The chemistry of manganese resembles in general that of chromium. The highest oxide (Mn₂O₇), in which the element shows its Group valency (7), is *acidic*, and the salts formed from this oxide (permanganates, *e.g.*, KMnO₄) are important oxidising agents. The lowest oxide (MnO) is basic and its derivatives (manganous salts, *e.g.*, MnSO₄) are reduction products of permanganates. An intermediate oxide (MnO₂) is stable, and is the only oxide likely to be met.

PERMANGANATES

The outstanding characteristics of permanganates (MnO₄⁻ ion) are their powerful oxidising action [1] and their deep violet colour, both in the solid state and in solution (*i.e.*, the MnO₄⁻ ion is violet). They are derived from the acid HMnO₄, the anhydride of which is the oxide Mn₂O₇; both of these are dangerously unstable, and of no practical importance.

When permanganates act as oxidising agents in *acid* solution [2] they are reduced to manganous salts (Mn++ ion, very pale pink, almost colourless).

$$MnO_4^- + 8H^+ + 5e = Mn^{++} + 4H_2O$$
$$2KMnO_4 = K_2O + 2MnO + 5(O).$$

An acidified solution of a permanganate oxidises the following, being itself reduced as shown above, and decolorised :

(a) chlorides, bromides, iodides and the corresponding acids to chlorine, bromine, iodine ;

(b) sulphides to sulphur ;

(c) sulphites to sulphates (SO₃⁻⁻ to SO₄⁻⁻) ;

(d) nitrites to nitrates (NO₂⁻ to NO₃⁻) ;

(e) ferrous to ferric salts (Fe++ to Fe+++) ;

(f) stannous to stannic salts (Sn++ to Sn++++) ;

(g) hydrogen peroxide ; all the available oxygen of both substances is liberated.

---

[1] Potassium and sodium permanganates are used as disinfectants ; the compounds presumably owe the value to the available oxygen present.
[2] For the use of potassium permanganate in volumetric analysis see pp. 153-155.

IONIC REACTIONS

Use potassium iodide (0·1M solution)

No.	Reagent	Visible Result	Comments
6	**Hydrogen** *Dil. HCl* . .	*None.*	*HI is strong and stable in these conditions.*
7	**Silver** AgNO₃ soln. .	Pale yellow ppt. AgI.	Insol in dil. HNO₃. Insol. in dil. NH₄OH.
8	**Barium** Ba(NO₃)₂ soln. .	None.	BaI₂ is sol.
9	**Lead** Lead acetate soln. .	Golden-yellow ppt. PbI₂.	Test more sensitive for I⁻ than for Cl⁻ or Br⁻. Ppt. sol. in much boiling water; crystallises as golden spangles on cooling.
10	**Mercuric** HgCl₂ soln. . .	Ppt. at first yellow, then pink, finally red, HgI₂.	See reactions of mercuric ion, p. 206.

OTHER IODINE COMPOUNDS

Non-metal iodides, apart from hydrogen iodide, are unimportant.

Hypoiodites (*e.g.*, NaIO) will be met as mild oxidising agents in organic chemistry (iodoform reaction, p. 335).

Iodates (*e.g.*, KIO₃) are used as standards in oxidation-reduction titrations (see p. 156). Potassium bi-iodate (KIO₃.HIO₃), being a stable solid acid salt, is useful as a primary standard in acid-base titrations (see pp. 142-143).

BIOLOGICAL RÔLE AND MEDICAL USES

'A most important naturally-occurring iodine compound is the am ino acid thyroxine, the hormone of the thyroid gland.

. . . . . septic (ti . . . . iodine, having a high atomic weight, is opaque to X-rays, and certain organic iodine compounds are used for rendering internal organs visible under X-rays.

IONIC REACTIONS

Use manganese sulphate (0·2M solution)

No.	Reagent	Visible Result	Comments
7	**Chloride** Dil. HCl . .	None.	$MnCl_2$ is sol.
8	**Sulphide** (a) H_2S+dil. HCl (b) H_2S+NH_4Cl +NH_4OH.	None. Pink ppt. MnS.	
9	**Hydroxide** (a) NaOH . .	White ppt. $Mn(OH)_2$.	Insol. in excess NaOH.
	(b) NH_4OH. .	,, ,,	Insol. in excess NH_4OH, but sol. in NH_4Cl.
10	**Carbonate** Na_2CO_3 or (NH_4)$_2CO_3$.	White ppt. $MnCO_3$.	

Analytical Behaviour.

Since the sulphide is insoluble in water but "soluble" in dilute acids, the manganous ion is in Class B in the Cation Separation. Since the hydroxide is not precipitated by ammonium hydroxide in the presence of ammonium chloride, the ion is in Group 4.

PERIODIC GROUP VIII

The metals of this group do not show their group valency except in a few compounds such as osmium tetroxide OsO_4. The three metals considered here—iron, cobalt and nickel—form cations with valencies of 2 and 3. They also form many complex anions.

9, 38   **IRON**

Valencies : 2, 3.
Oxides : FeO, Fe_3O_4, Fe_2O_3.
Cations : Fe^{++}, ferrous ; Fe^{+++}, ferric.
Anions : [Fe(CN)$_6$]$^{----}$, ferrocyanide.
            [Fe(CN)$_6$]$^{---}$, ferricyanide.

Iron is a heavy magnetic metal (m.p.=1500° ; d=7·8). It does not react with cold dry air, but "rusts" in moist air to form a hydrated ferric oxide (Fe_2O_3+H_2O). Iron combines directly on heating with sulphur (see p. 247) and with chlorine (see p. 259).

$$Fe+S = FeS ; 2Fe+3Cl_2 = 2FeCl_3.$$
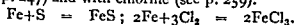
1. Acidify potassium permanganate solution (0·1M) with dilute sulphuric acid and add sulphurous acid. The violet colour of the permanganate is discharged. The reactions with the other reducing agents listed above may be carried out similarly.

When permanganates act as oxidising agents in *alkaline* solution, they are reduced to manganese dioxide, MnO_2.

$$2KMnO_4 = K_2O + 2MnO_2 + 3(O).$$
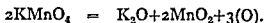
Examples of this reaction will be met in organic chemistry (p. 317). The reaction between permanganates and concentrated sulphuric acid is *dangerously violent and must not be tried*.

All permanganates are soluble in water; precipitation tests therefore cannot be used to identify the ion.

MANGANESE DIOXIDE

This oxide (MnO_2), which is a black solid insoluble in water, is a peroxide. On heating it evolves oxygen (with difficulty), and on heating with hydrochloric acid, it oxidises the latter to chlorine.

$$MnO_2 + 4HCl = MnCl_2 + Cl_2 + 2H_2O.$$
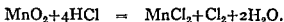
2. Heat manganese dioxide alone.
3. Heat manganese dioxide with dilute hydrochloric acid.

MANGANOUS SALTS

The oxide will not be met. The hydroxide $Mn(OH)_2$ is white, but is rapidly oxidised in air to brown hydrated manganese dioxide. The manganous ion Mn^{++} is very pale pink and many solid compounds are pink.

All manganese compounds are reduced in the charcoal block test to the metal. In the borax bead test all manganese compounds give a violet bead in the oxidising flame and a colourless bead in the reducing flame.

Manganous compounds are oxidised by red lead and nitric acid to permanganates.

$$2Mn^{++} + 4H^+ + 5PbO_2 = 5Pb^{++} + 2H_2O + 2MnO_4^-.$$
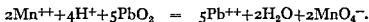
4, 5. Use manganous sulphate for the charcoal block and borax bead tests.
6. To manganous sulphate solution (1 ml.) add red lead (1 spatula-point) and concentrated nitric acid, and boil. Allow the excess lead peroxide to settle, and note the deep pink colour of the supernatant liquid due to permanganate ions.

Solubility of Salts.

Halides, sulphate, nitrate .	Soluble in water.
Sulphide, carbonate .	Insoluble in water, " soluble " in dilute acids.

Ferric compounds are reduced to ferrous compounds by the following reagents :

(f) nascent hydrogen ;
(g) hydrogen sulphide ;
(h) sulphurous acid ;
(i) hydriodic acid (acidified potassium iodide solution) ;
(j) stannous chloride.

6. (a) Show that a stock solution of ferrous sulphate contains ferric ions,

with the reagents named

reagents listed above and

note the results.

FERROUS SALTS

Solubilities.

Halides, sulphate, nitrate.	Soluble in water.
Sulphide, carbonate [1]	Insoluble in water, " soluble " in dilute acids.

IONIC REACTIONS
Use ferrous sulphate (0·2M solution)

No.	Reagent	Visible Result	Comments
8	Chloride Dil. HCl . .	None.	$FeCl_2$ is sol.
9	Sulphide (a) H_2S+dil. HCl (b) H_2S+NH_4OH +NH_4Cl.	None Black ppt. FeS.	
10	Hydroxide (a) NaOH . . (b) NH_4OH .	Dirty green ppt. $Fe(OH)_2$+$Fe(OH)_3$. ,, ,,	$Fe(OH)_2$ is sol. in NH_4Cl.
11	Carbonate Na_2CO_3 or $(NH_4)_2CO_3$.	White ppt. $FeCO_3$.	
12	Ferrocyanide $K_4[Fe(CN)_6]$.	White ppt. $K_2Fe[Fe(CN)_6]$.	Usually pale blue, due to ferric salt.
13	Ferricyanide $K_3[Fe(CN)_6]$.	Dark blue ppt. $KFe[Fe(CN)_6]$.	
14	Thiocyanate KSCN . .	None.	Contrast ferric ion.

[1] The carbonate is also "soluble" in carbonic acid solution, due to the formation of a bicarbonate, $Fe(HCO_3)_2$.

Iron does not react with cold water, but displaces hydrogen from dilute mineral acids forming ferrous salts.

$$Fe + 2H^+ \;=\; Fe^{++} + H_2\!\uparrow.$$

Concentrated nitric acid does not "dissolve" iron. The metal becomes covered with an impermeable layer of oxide, which protects it from further oxidation. Iron, being higher in the electrochemical series than copper, displaces the latter from its salts.

$$Fe + Cu^{++} \;=\; Cu + Fe^{++}.$$
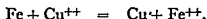
1. Remove all rust from two iron nails, I and II. Place them in tubes

Nail II is exposed to water and oxygen; it rusts. Nail I is exposed to oxygen but not water; it does *not* rust.

2. Treat iron filings with dilute sulphuric acid.

3. Place a bright iron nail in copper sulphate solution. The nail becomes covered with a pink film of copper.

Ferrous oxide (FeO, black) will not be met. The hydroxide $Fe(OH)_2$, which is a weak base, is said to be white when pure ; it oxidises very rapidly in air, and sodium hydroxide precipitates from ferrous salt solutions a dirty green precipitate which rapidly turns brown (formation of ferric hydroxide). Ferric oxide Fe_2O_3 and the hydroxide $Fe(OH)_3$, which is a very weak base, are reddish brown solids, insoluble in water but readily "soluble" in dilute acids. These and other iron compounds may be reduced to the metal by heating with carbon.

Iron gives coloured borates in the borax bead test, viz. :—green ferrous borate in the reducing flame, yellow ferric borate in the oxidising flame.

4, 5. Use ferrous sulphate for charcoal block and borax bead tests.

Iron forms two fairly stable series of salts (ferrous and ferric, Fe^{++} and Fe^{+++} ions) which are readily interconvertible.

$$Fe^{++} \;\rightleftharpoons\; Fe^{+++} + e.$$
$$\text{(pale green)} \qquad \text{(yellow)}$$
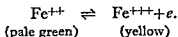
Ferrous compounds are oxidised to ferric compounds by the following reagents :

(a) atmospheric oxygen (the ion and some solid compounds slowly ; the oxide and hydroxide rapidly. All ordinary samples of ferrous compounds are therefore contaminated with ferric compounds) ;

(b) chlorine ;

(c) dilute nitric acid (hot) ;

(d) acidified permanganate [1] ;

(e) acidified dichromate.

[1] Used for the volumetric determination of iron, see p. 155.

Analytical Behaviour.

Since ferric sulphide is insoluble in water but decomposed by dilute acids, the ferric ion is in Class B of the Cation Separation. Since the hydroxide is precipitated by ammonium hydroxide in the presence of ammonium chloride, the ion is in Group 3.

FERROCYANIDES

The ferrocyanide ion $[Fe(CN)_6]$————, which may be formed by treating a ferrous salt with an excess of cyanide (see p. 218), is so stable that its compounds give none of the reactions of ferrous or of cyanide ions. It is chiefly important here as a reagent for cations.

The salts show no visible reaction with dilute hydrochloric acid; with hot concentrated sulphuric acid, carbon monoxide is evolved (compare cyanides, p. 218). The ion is very pale yellow; the soluble salts (those of Na, K, Ca and Ba) are yellow; the insoluble salts (all others) are variously coloured.

IONIC REACTIONS

Use potassium ferrocyanide (0·2M solution)

No.	Reagent	Visible Result	Comments
23	**Hydrogen** Dil. HCl	None.	
24	**Silver** AgNO₃	White ppt. Ag₄[Fe(CN)₆].	Insol. in dil. HNO₃.
25	**Barium** Ba(NO₃)₂	None.	Ba₂Fe(CN)₆ is sol.
26	**Ferrous** FeSO₄	White ppt. Ferrous ferrocyanide K₂Fe[Fe(CN)₆].	This ppt. is always pale blue, due to contamination of ferrous with ferric salts.
27	**Ferric** FeCl₃	Prussian blue ppt. ferric ferrocyanide KFe[Fe(CN)₆].	
28	**Cupric** CuSO₄	Brown ppt. Cu₂[Fe(CN)₆].	

FERRICYANIDES

The stability of the ferricyanide ion $[Fe(CN)_6]$———, which may be formed by treating a solution of a ferric salt with an excess of cyanide solution, is similar to that of the ferrocyanide ion.

Analytical Behaviour.

Since ferrous sulphide is insoluble in water but " soluble " in dilu acids, the ferrous ion is in Class B of the Cation Separation.

Ferrous hydroxide is soluble in ammonium chloride solution ar the ferrous ion is, strictly speaking, in Group 4. Ferrous salts ar however, nearly always contaminated with ferric salts, which a precipitated as hydroxide by ammonium hydroxide and ammoniu chloride. It is therefore customary in analysis to oxidise ferrous sal with nitric acid to ferric salts, so that all the iron is precipitated b the Group 3 reagent.

FERRIC SALTS

Solubilities.

Chloride, bromide, sulphate, nitrate. Soluble in water.
Basic carbonate, sulphide . . Insoluble in water, readily de composed.
Iodide . . . . . Does not exist.

IONIC REACTIONS
Use ferric chloride (0·2M solution)

No.	Reagent	Visible Result	Comments
15	Chloride Dil. HCl . .	None.	FeCl₃ is sol.
16	Sulphide (a) H₂S+dil. HCl (b) H₂S+NH₄Cl +NH₄OH.	Faint yellow ppt. S. Black ppt. Fe₂S₃.	H₂S is oxidised.
17	Hydroxide (a) NaOH . . (b) NH₄OH.	Red-brown ppt. Fe(OH)₃. ,, ,,	Insol. in excess NH₄OH or NH₄Cl.
18	Carbonate Na₂CO₃ or (NH₄)₂CO₃.	Red-brown ppt. Fe(OH)₃.	Ferric carbonate does not exist.
19	Ferrocyanide K₄[Fe(CN)₆] .	Prussian blue ppt. KFe[Fe(CN)₆].	
20	Ferricyanide K₃[Fe(CN)₆] .	No ppt. Brown colour.	
21	Acetate CH₃COONa .	Deep red colour.	Due to complex ion.
22	Thiocyanate KSCN . .	Very deep red colour.	Due to complex ion [Fe(SCN)₆]———.

Cobalt compounds are reduced on the charcoal block to metal. In the borax bead they form a blue borate.

The oxidation of divalent to trivalent cobalt is illustrated by the formation of cobaltic oxide Co_2O_3 with hypochlorite (p. 261) and of potassium cobaltinitrite with potassium nitrite and acetic acid.

$$Co^{++} - e = Co^{+++}.$$

1, 2. Use cobalt nitrate for charcoal block and borax bead tests.

3. Acidify cobalt nitrate solution (1 ml.) with dilute acetic acid (5 drops). Add potassium nitrite solution (2 ml.). A yellow precipitate of potassium cobaltinitrite is formed.

Solubilities of Cobaltous Salts.

Halides, sulphate, nitrate.	Soluble in water.
Carbonate, sulphide .	Insoluble in water, " soluble " in dilute acids.

IONIC REACTIONS

Use cobalt nitrate (0·2M solution)

No.	Reagent	Visible Result	Comments
4	Chloride Dil. HCl . .	None.	$CoCl_2$ is sol.
5	Sulphide (a) H_2S+dil. HCl (b) H_2S+NH_4Cl +NH_4OH.	None. Black ppt. CoS.	
6	Hydroxide (a) NaOH . . (b) NH_4OH . .	Blue basic salt or pink $Co(OH)_2$ pptd. Blue basic salt pptd.	Insol. in excess NaOH. Sol. in excess NH_4OH or in NH_4Cl due to formation of complex ion.
7	Carbonate (a) Na_2CO_3 . (b) $(NH_4)_2CO_3$.	Mauve ppt. $CoCO_3$ (basic). " "	Sol. in excess $(NH_4)_2CO_3$ or NH_4OH, giving *purple solution containing complex ion.*

Analytical Behaviour.

Since cobalt sulphide is insoluble in water but " soluble " in dilute acid, cobalt is in Class B in the Cation Separation. Since the hydroxide is not precipitated by ammonia and ammonium chloride it is in Group 4.

The salts behave like ferrocyanides with dilute hydrochloric acid and concentrated sulphuric acid. The ion is greenish-yellow; the soluble salts (those of Na, K, Ca, Ba and Fe^{+++}) are reddish-brown; the insoluble salts (all others) are variously coloured.

IONIC REACTIONS

Use potassium ferricyanide (0·2M solution)

No.	Reagent	Visible Result	Comments
29	Hydrogen Dil. HCl . .	None.	. .
30	Silver AgNO₃ . .	Orange ppt. Ag₃[Fe(CN)₆].	Insol. in dil. HNO₃.
31	Barium Ba(NO₃)₂ . .	None.	Ba salt is sol.
32	Ferrous FeSO₄ . .	Dark blue ppt. Ferrous ferricyanide KFe[Fe(CN)₆].	.
33	Ferric FeCl₃ . .	Brown soln.	

BIOLOGICAL RÔLE AND MEDICAL USES

Iron is an essential constituent of the mammalian body, the pigment of red blood corpuscles being an organic compound containing iron (haemoglobin, see pp. 410–411).

Ferrous sulphate, ferrous carbonate and ferric ammonium citrate are used in the treatment of certain kinds of anaemia. Ferric chloride is used as an astringent since, like other heavy metals, iron is a protein precipitant.

9, 39   COBALT

Valencies : 2, 3.   *Oxides :* CoO, Co₂O₃.   *Cation :* Co⁺⁺.

The important simple compounds of cobalt are those in which the metal is divalent, cobaltous compounds, giving the ion Co⁺⁺. The ion and hydrated solid compounds are pink; some anhydrous salts are blue. The colour change on hydration may be used to detect water (see p. 245).

. Cobalt forms many complex compounds, in some of which it is trivalent. These complexes include compounds formed with ammonia and with various anions (nitrite, thiocyanate, etc.). The solubility of many cobaltous compounds in ammonia is due to the formation of complexes (see reactions 6 and 7).

Cobalt compounds are reduced on the charcoal block to metal. In the borax bead they form a blue colour.

The oxidation of divalent to trivalent cobalt is illustrated by the formation of cobaltic oxide Co_2O_3 with hypochlorite (p. 261) and of potassium cobaltinitrite with potassium nitrite and acetic acid.

$$Co^{++} - e = Co^{+++}.$$

1, 2. Use cobalt nitrate for charcoal block and borax bead tests.

3. Acidify cobalt nitrate solution (1 ml.) with dilute acetic acid (5 drops). Add potassium nitrite solution (2 ml.). A yellow precipitate of potassium cobaltinitrite is formed.

Solubilities of Cobaltous Salts.

Halides, sulphate, nitrate. Soluble in water.
Carbonate, sulphide   . Insoluble in water, " soluble " in dilute acids.

IONIC REACTIONS
Use cobalt nitrate (0·2M solution)

No.	Reagent	Visible Result	Comments
4	**Chloride** Dil. HCl .	None.	$CoCl_2$ is sol.
5	**Sulphide** (a) H_2S+dil. HCl (b) H_2S+NH_4Cl +NH_4OH.	None. Black ppt. CoS.	
6	**Hydroxide** (a) NaOH . (b) NH_4OH .	Blue basic salt or pink $Co(OH)_2$ pptd. Blue basic salt pptd.	Insol. in excess NaOH. Sol. in excess NH_4OH or in NH_4Cl due to formation of complex ion.
7	**Carbonate** (a) Na_2CO_3 . (b) $(NH_4)_2CO_3$.	Mauve ppt. $CoCO_3$ (basic). " "	Sol. in excess $(NH_4)_2CO_3$ or NH_4OH, giving purple solution containing complex ion.

Analytical Behaviour.

Since cobalt sulphide is insoluble in water but " soluble " in dilute acid, cobalt is in Class B in the Cation Separation. Since the hydroxide is not precipitated by ammonia and ammonium chloride it is in Group 4.

BIOLOGICAL RÔLE

Cobalt (in very small quantities) is essential for many mammals (including probably man); it is probably concerned with the formation of red blood cells.

9, 40   NICKEL

Valency: 2.   *Oxide:* NiO.   *Cation:* Ni⁺⁺.

Nickel closely resembles cobalt in its chemistry, except in the colours of its compounds (the hydrated Ni^{++} ion and solid hydrated salts are green), and in being divalent in all its important compounds (both simple and complex).

Nickel compounds on heating with charcoal yield the metal; in the borax bead they form a brown borate in the oxidising flame and grey metallic nickel in the reducing flame. Nickel does not form a complex nitrite (contrast cobalt).

The solubilities of the common salts and the analytical behaviour of the cation are as detailed for cobalt.

1, 2. Use nickel sulphate for charcoal block and borax bead tests.

IONIC REACTIONS
Use nickel sulphate (0·2M solution)

No.	Reagent	Visible Result	Comments
3	**Chloride** Dil. HCl .	None.	$NiCl_2$ is sol.
4	**Sulphide** (a) H_2S+dil. HCl (b) H_2S+NH_4Cl +NH_4OH.	None. Black ppt. NiS.	
5	**Hydroxide** (a) NaOH . . (b) NH_4OH .	Pale-green ppt. $Ni(OH)_2$. Pale-green ppt., basic salt.	Insol. in excess NaOH. Sol. in excess NH_4OH or in NH_4Cl, giving deep blue soln. containing complex ion.
6	**Carbonate** (a) Na_2CO_3 . (b) $(NH_4)_2CO_3$	Pale green ppt. $NiCO_3$. ,, ,,	Sol. in excess $(NH_4)_2CO_3$ or in NH_4OH, giving deep blue soln. containing complex ion.

FURTHER READING

DESCRIPTIVE INORGANIC CHEMISTRY

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HOLMYARD, E. J. Higher School Certificate Inorganic Chemistry. Arnold, London, 1939.

CAVEN, R. M. and LANDER, G. D. Systematic Inorganic Chemistry, 6th edition revised by CRAWFORD, A. B. Blackie, London, 1939.

DURRANT, P. J. General and Inorganic Chemistry. Longmans, Green, London, 1939.

PARTINGTON, J. R. A Text-Book of Inorganic Chemistry, 5th edition. Macmillan, London, 1943.

EPHRAIM, F. A Text-Book of Inorganic Chemistry. English edition by THORNE, P. C. L., and ROBERTS, E. R. Gurney and Jackson, Edinburgh, 1946.

(Any of these books includes *more* inorganic chemistry than is required for a first-year medical course.)

REACTIONS USED IN QUALITATIVE ANALYSIS

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VOGEL, A. I. A Text-Book of Qualitative Chemical Analysis, 3rd edition. Longmans, Green, London, 1945.

TREADWELL, F. P. Analytical Chemistry, vol. I., Qualitative Analysis, 9th English edition, translated and revised by HALL, W. T. Wiley, New York, 1937.

BIOLOGICAL RÔLE

Cobalt (in very small quantities) *is essential for many mammals* (including probably man) ; it is probably concerned with the formation of red blood cells.

9, 40 NICKEL

Valency : 2. Oxide : NiO. Cation : Ni++.

Nickel closely resembles cobalt in its chemistry, except in the colours of its compounds (the hydrated Ni++ ion and solid hydrated salts are green), and in being divalent in all its important compounds (both simple and complex).

Nickel compounds on heating with charcoal yield the metal ; in the borax bead they form a brown borate in the oxidising flame and grey metallic nickel in the reducing flame. Nickel does not form a complex nitrite (contrast cobalt).

The solubilities of the common salts and the analytical behaviour of the cation are as detailed for cobalt.

1, 2. Use nickel sulphate for charcoal block and borax bead tests.

IONIC REACTIONS

Use nickel sulphate (0·2M solution)

No.	Reagent	Visible Result	Comments
3	**Chloride** Dil. HCl . .	None.	$NiCl_2$ is sol.
4	**Sulphide** (a) H_2S+dil. HCl (b) H_2S+NH_4Cl +NH_4OH.	None. Black ppt. NiS.	
5	**Hydroxide** (a) NaOH . . . (b) NH_4OH .	Pale-green ppt. $Ni(OH)_2$. Pale-green ppt., basic salt.	Insol. in excess NaOH. Sol. in excess NH_4OH or in NH_4Cl, giving deep blue soln. containing complex ion.
6	**Carbonate** (a) Na_2CO_3 . (b) $(NH_4)_2CO_3$.	Pale green ppt. $NiCO_3$. ,, ,,	Sol. in excess $(NH_4)_2CO_3$ or in NH_4OH, giving deep blue soln. containing complex ion.

Anions—*continued*.

Bromide	Thiosulphate	Arsenate	Ferricyanide
Iodide	Chromate	Carbonate	
Permanganate	Dichromate	Cyanide	

METHOD

The method falls into three parts, viz.: (1) a brief preliminary examination, (2) identification of the anion, (3) identification of the cations. Parts (2) and (3), which are almost independent of one another, demand the preparation of an aqueous solution from the substance.[1]

Preliminary Examination.

This consists only of the examination of the appearance and smell of the substance, and tests of its solubility in water and behaviour towards litmus.[2]

Identification of the Anion.

The method involves, first, the application of four general tests, which together identify many anions. These tests are:

(1) Treatment with dilute hydrochloric acid.
(2) Treatment with concentrated sulphuric acid.
(3) Treatment of an aqueous solution with silver nitrate solution.
(4) Treatment of any precipitate formed in (3) with dilute nitric acid.

Tests (1) and (2) depend on the strength, stability and volatility of the acids corresponding to the anions (see pp. 108-109); tests (3) and (4) depend on the solubilities of the silver salts of the acids (see pp. 88-89).

Subsequently, specific tests must be applied to distinguish between anions which behave in the same way with the general reagents, and finally confirmatory tests must be carried out.

[1] The ....
list is $27 \times 26 = 702$. If anions and cations did not behave independently in aqueous solution, it would be necessary to find specific tests for every one of these 702 compounds. Since in fact the ions do behave independently in solution, it is necessary to distinguish only $27 + 26 = 53$ entities.

[2] Many books include here a number of dry tests—behaviour on heating, flame, charcoal block and borax bead tests. The author considers it more economical of the student's time to use these as confirmatory tests *after* the wet analysis, since results of the dry tests are rarely as definite as those of the wet tests.

IDENTIFICATON OF SIMPLE INORGANIC SUBSTANCES

10, 1   **INTRODUCTION**

PURPOSE AND SCOPE OF WORK

This work has two objects, viz.: (1) to give the student practice in the application of some of the commoner inorganic reactions, (2) to give practice in logical deduction. The scheme outlined in this chapter will enable the student to identify single substances giving rise in solution to the ions listed below.[1] The scheme will *not* serve for the identification of mixtures, although it is based on more elaborate methods used for the examination of these.

All compounds insoluble in dilute acids, and phosphates insoluble in water, are excluded from the scope of the systematic identification method because of special difficulties involved. A brief note on the examination of these substances is given on pp. 292-293.

IONS INCLUDED

Cations.

Hydrogen	Calcium	Aluminium	Chromic
Sodium	Strontium	Stannous	Manganous
Potassium	Barium	Stannic	Ferrous
Ammonium	Zinc	Lead	Ferric
Cupric	Cadmium	Arsenious	Cobalt
Silver	Mercurous	Antimony	Nickel
Magnesium	Mercuric	Bismuth	

Anions.

Fluoride	Hydroxide	Nitrite	Thiocyanate
Chloride	Sulphide	Nitrate	Silicate
Hypochlorite	Sulphite	Phosphate	Borate
Chlorate	Sulphate	Arsenite	Ferrocyanide

[1] The selection of ions is that prescribed by custom for elementary books. Many instructors (the author among them) will exclude some of these from their courses.

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The following form of report is suggested : ʼ

27 Nov. 1945. Identification of Substance No. 20. ·

Reason for Test	Test[1]	Observation	Conclusion[2]
Preliminary examination.	Appearance.	White crystalline solid.	Cu, Fe, Cr, Mn, Co, Ni probably absent.
	Solubility in water.	Readily sol. in cold; soln. colourless.	
	Soln. in water prepared; called O.S. Behaviour of soln. with litmus.	Slightly acidic.	Acid or hydrolysed salt.
Identification of Anion: General Tests.	Substance+dil. HCl.	No action.[3]	} Probably sulphate.
	Substance+conc. H₂SO₄.	,,	
	O.S.+AgNO₃ soln.	,,	
Special and Confirmatory Tests.	O.S.+Ba(NO₃)₂ soln.	White ppt. insol. in dil. HNO₃.	SULPHATE present.
	O.S.+lead acetate soln.	White ppt.	SULPHATE confirmed.
Identification of Cation : Group Tests.	O.S +dil HCl.	No ppt.[3]	Group 1 absent.
	O.S+dil. HCl+ H₂S.	,,	,, 2 ,,
	O.S.+NH₄Cl+ NH₄OH.	,,	,, 3 ,,
	Ditto+H₂S.	White ppt.	,, 4 present.
Special and Confirmatory Tests	—	—	Colour of Group ppt. indicates ZINC present.
	O S.+NaOH soln.	White ppt. sol. in excess.	ZINC confirmed.
	Substance heated on charcoal block with Na₂CO₃.	Residue yellow hot, white cold.	ZINC confirmed.

CONCLUSION. Substance No. 20 is ZINC SULPHATE.[4]

Points to Note.

1. The material used for each test, *e.g.*, " substance." " O.S." (defined as an aqueous solution of the substance) is stated.

2. A sharp distinction is drawn between *certainties* (" Group 1 absent ") and *possibilities* or *probabilities* (" Cu, etc. probably absent ").

3. *Negative evidence* plays a very large part in the identification.

4. The final *conclusion* is stated *boldly*.

Identification of the Cation.

The first stage in the identification of the cation is the " Group Separation," a method which determines to which of a number of small groups the cation belongs. The logic and the chemistry of the Group Separation have been discussed in chapter 2 (pp. *11-12*) and chapter 6 (pp. *90-91*) respectively.

Subsequently, specific tests must be applied to distinguish between cations which behave in the same way with the Group reagents, and finally confirmatory tests must be carried out.

The majority of the cation tests are precipitation reactions.

IMPURITIES

Samples provided for identification will, as far as possible, be of such quality that any impurities present will not interfere with the usual tests. There are, however, some compounds which it is very difficult to provide and keep free from interfering substances.

These are in many cases formed by the action on the original substance of atmospheric constituents (oxygen, water, carbon dioxide) or of containers (*e.g.*, silicates from glass).

Class of Substances	Impurities	Cause
Metallic oxides and hydroxides.	Carbonates.	CO_2 of atmosphere.
Alkaline solutions {	Carbonates.	CO_2 of atmosphere.
	Silicates.	Glass.
Ferrous salts . .	Ferric salts.	Oxygen of atmosphere.
Sulphites . .	Sulphates.	,, ,,
Many solutions .	Sodium (trace).	Glass.

The student must use his judgment in deciding whether a positive result in a test is such that it is probably due to the main substance present, or to a trace of impurity.

10, z   **REPORTS**

The reason for applying each test, the nature of the test, the results and the conclusions drawn from them must be written in a note-book *immediately* the test has been done. It must be realised that negative evidence—the fact that a substance gives *no* visible change with a certain reagent—is just as important as positive evidence.

The following form of report is suggested : '

27 Nov. 1945. Identification of Substance No. 20.

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	Solubility in water.	Readily sol. in cold; soln. colourless.	
	Soln. in water prepared; called O.S. Behaviour of soln. with litmus.	Slightly acidic.	Acid or hydrolysed salt.
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	O.S.+AgNO₃ soln.	,,	
Special and Confirmatory Tests.	O.S.+Ba(NO₃)₂ soln.	White ppt. insol. in dil. HNO₃.	SULPHATE present.
	O.S.+lead acetate soln.	White ppt.	SULPHATE confirmed.
Identification of Cation : Group Tests.	O.S.+dil. HCl.	No ppt.[3]	Group 1 absent.
	O.S.+dil. HCl+ H₂S.	,,	,, 2 ,,
	O.S.+NH₄Cl+ NH₄OH.	,,	,, 3 ,,
	Ditto+H₂S.	White ppt.	,, 4 present.
Special and Confirmatory Tests.	—	—	Colour of Group ppt. indicates ZINC present.
	O.S.+NaOH soln.	White ppt. sol in excess.	ZINC confirmed.
	Substance heated on charcoal block with Na₂CO₃.	Residue yellow hot, white cold.	ZINC confirmed.

CONCLUSION. Substance No. 20 is ZINC SULPHATE.[4]

Points to Note.

1. The material used for each test, *e.g.*, "substance." "O.S." (defined as an aqueous solution of the substance) is stated.

2. A sharp distinction is drawn between *certainties* ("Group 1 absent") and *possibilities* or *probabilities* ("Cu, etc. probably absent").

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4. The final *conclusion* is stated *boldly*.

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Subsequently, specific tests must be applied to distinguish between cations which behave in the same way with the Group reagents, and finally confirmatory tests must be carried out.

The majority of the cation tests are precipitation reactions.

IMPURITIES

Samples provided for identification will, as far as possible, be of such quality that any impurities present will not interfere with the usual tests. There are, however, some compounds which it is very difficult to provide and keep free from interfering substances.

These are in many cases formed by the action on the original substance of atmospheric constituents (oxygen, water, carbon dioxide) or of containers (e.g., silicates from glass).

Class of Substances	Impurities	Cause
Metallic oxides and hydroxides.	Carbonates.	CO_2 of atmosphere.
Alkaline solutions {	Carbonates. Silicates.	CO_2 of atmosphere. Glass.
Ferrous salts . .	Ferric salts.	Oxygen of atmosphere.
Sulphites . .	Sulphates.	,, ,,
Many solutions .	Sodium (trace).	Glass.

The student must use his judgment in deciding whether a positive result in a test is such that it is probably due to the main substance present, or to a trace of impurity.

10, 2   **REPORTS**

The reason for applying each test, the nature of the test, the results and the conclusions drawn from them must be written in a note-book immediately the test has been done. It must be realised that negative evidence—the fact that a substance gives no visible change with a certain reagent—is just as important as positive evidence.

A. A liquid which is *acid* to litmus contains either an acid, *e.g.*, sulphuric acid, or a hydrolysed salt formed from a strong acid and a weak base, *e.g.*, copper sulphate.

B. A liquid which is *alkaline* to litmus contains either a base, *e.g.*, sodium hydroxide, or a hydrolysed salt formed from a weak acid and a strong base, *e.g.*, sodium carbonate.

C. A liquid which is *neutral* to litmus certainly does *not* contain either an acid or a base.

Note particularly that if the liquid is acid or alkaline to litmus, this does *not* mean that the " unknown " is necessarily an acid or a base. See pp. 95–96 regarding hydrolysis of salts.

IDENTIFICATION OF THE ANION

10, 4   GENERAL TESTS

The four general tests, as stated previously, are :

1. Treatment with dilute hydrochloric acid.
2. Treatment with concentrated sulphuric acid.
3. Treatment of an aqueous solution with silver nitrate solution.
4. Treatment of precipitates formed in (3) with dilute nitric acid.

The results given by the different anions are detailed in the table on p. 284.

The tests, materials and quantities to be used are as follows :

Liquid Unknowns.

Test 1. Unknown (1 ml.), dil. HCl (1 ml.) ; warm if there is no visible action in the cold.

Test 2. *Do this test only if there is no visible action in Test 1.* Unknown (1 ml.), conc. H_2SO_4 (2 ml.) ; heat if there is no visible action in the cold.

Test 3. Unknown (1 ml.), $AgNO_3$ solution (1 ml.).

Test 4. Do this test only if there is a precipitate in Test 3. Acidify the reaction mixture from Test 3 with dil. HNO_3.

Solid Unknowns Soluble in Water.

Test 1. Unknown (2 spatula-points), dil. HCl (1 ml.) ; warm if there is no visible action in the cold.

Test 2. *Do this only if there is no visible action in Test 1.* Unknown (2 spatula-points), conc. H_2SO_4 (1 ml.) ; heat if there is no visible action in the cold.

Tests 3 and 4. As for liquids, using aqueous solution of unknown (1 ml.).

Solid Unknowns Insoluble in Water, " Soluble " in Dilute Acid.

Tests 1 and 2. As for water-soluble solids.

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[1] In more advanced work it would be necessary to carry out further tests.

10, 3   PRELIMINARY EXAMINATION AND PREPARATION OF SOLUTION

Appearance.

Note the appearance (state, colour, crystalline form) and smell (if any) of the substance to be identified (the "unknown "). These properties may give useful clues as to the nature of the substance. Do *not* allow first impressions to prejudice your interpretation of later results.

It may be assumed that liquids given for examination are aqueous solutions.

> *Nearly all solid* compounds of the following elements are *coloured*; their *ions* (and therefore solutions of their compounds) are *coloured* :—copper, iron, chromium, manganese, cobalt, nickel.
>
> *Some* solid compounds of the following elements are *coloured*; but their *ions* (and therefore solutions of their compounds) are *colourless* :—silver, mercury, lead, arsenic, antimony, bismuth, cadmium.
>
> *All solid* compounds of the following elements are *colourless*[1]; their *ions* (and therefore solutions of their salts) are *colourless* :—aluminium, zinc, calcium, strontium, barium, magnesium, sodium, potassium, hydrogen (also ammonium compounds).

Tests on Solubility.

Test the solubility of the substance (if solid) in the common solvents in the following order until you find one in which the substance is soluble : (1) water, (2) dilute hydrochloric acid, (3) dilute nitric acid. Note the colour (if any) of the solution.

> Add the substance (1 spatula-point) to the solvent (5 ml.) and stir with a glass rod. If the substance does not dissolve in the cold, heat gently to boiling. If the substance still does not dissolve, it may be considered insoluble, and the next solvent tried.

Preparation of a Solution for Tests.

A 5-10% solution of the "unknown" in water (or dilute acid if necessary) will be found most suitable for carrying out tests. A ⎧ ⎫ : (10 ml.). warming and shaking, or if it dissolves on warming and solid separates again on cooling, add more solvent until all the solid dissolves or filter off the undissolved solid. Never use a mixture of solvent and undissolved solid for tests which are supposed to be carried out in solution. In the first place you cannot tell whether any of the "unknown" is in solution; in the second place you will be unable to observe the formation of precipitates in the solution, because solid is already present.

Reaction to Litmus.

Test with litmus-paper (*not* solution) liquid "unknowns," and the solutions of *water-soluble* solid "unknowns."

[1] Unless they also contain "coloured" elements, *e.g.*, manganese in permanganates.

10, 5   SPECIAL AND CONFIRMATORY TESTS

Anion	Tests	For details see pp.
Fluoride	Silicon fluoride, barium [1]	257-258
Chloride	⎫ Distinguish between the three halide ions ⎧	260
Bromide	⎬ by chlorine water. Other tests: lead ⎨	263
Iodide	⎭ mercuric (iodide only) . . ⎩	265-266
Hypochlorite	Catalytic decomposition by cobalt salt	261
Chlorate	Heat	261
Permanganate	Colour, reduction by ferrous salt or hydrogen sulphide. Borax bead	267-268
Hydroxide	Litmus, mercuric	246
Sulphide	Lead. Nitroprusside . . .	248-249
Sulphite	Oxidation to sulphate. Decolorisation of permanganate. Heat . . .	250
Sulphate	Lead, barium	252
Thiosulphate	Reduction of iodine . . .	252
Chromate	⎫ Colour of solution. Reduction by sulphur-	
Dichromate	⎬ ous acid. Borax bead . . .	254-256
Nitrite	Brown ring test (in presence of acetic acid) .	232
Nitrate	Brown ring test (in presence of conc. H_2SO_4). Heat	233
Phosphate	Molybdate test. Distinction between three types of phosphate by barium . .	236
Arsenite	Copper (reduction). Precipitation of As_2S_3 by dil. HCl and H_2S . . .	238-239
Arsenate	Reduction and precipitation of As_2S_3 by dil. HCl and H_2S. Molybdate . .	240
Carbonate	Calcium, barium. Heat . . .	216-217
Cyanide	Formation of Prussian blue . .	218
Thiocyanate	Ferric	220
Silicate	Barium	221
Borate	Esterification. Turmeric . .	208-209
Ferrocyanide	Ferric, cupric	273
Ferricyanide	Ferrous	274
(Normal oxide)	None	—
(Peroxide)	Heat	—
(Metal)	Nitric acid	—

[1] Ionic precipitation reactions are indicated by the name of the cation to be used.

GENERAL TESTS FOR ANIONS

Anion	Visible Results of Tests			
	1 Dil. HCl	**2** Conc. H_2SO_4	**3** $AgNO_3$	**4** $AgNO_2$+HNO_2
Fluoride . .	None.	$HF\uparrow.$	None.	•
Chloride . .	None.	$HCl\uparrow.$	White ppt.	Insol.
Hypochlorite .	$Cl_2\uparrow.$	$Cl_2\uparrow.$	(White ppt.²)	(Insol.²)
Chlorate . .	None.	Cl_2+$ClO_2\uparrow.$	None.	•
Bromide . .	None.	HBr+$Br_2\uparrow.$	Cream ppt.	Insol.
Iodide . .	None.	HI+$I_2\uparrow.$	Pale yellow ppt.	Insol.
Permanganate .	$Cl_2\uparrow.$	•	None.	•
Hydroxide . .	None.	None.	Brown ppt.	Sol.
Sulphide . .	$H_2S\uparrow.$	•	Black ppt.	Insol.
Sulphite . .	$SO_2\uparrow.$	•	White ppt.	Sol.
Sulphate . .	None.	None.	None.	•
Thiosulphate .	SO_2+$S\downarrow.$	•	White ppt.⁴	•
Chromate . .	Red colour.	Deep red soln.	Red ppt.	Sol.
Dichromate .	None.	Deep red soln.	Red ppt.	Sol.
Nitrite . .	$NO_2\uparrow.$	•	None.	•
Nitrate . .	None.	$NO_2\uparrow.$	None.	•
Phosphate ¹ .	None.	None.	Yellow ppt.	Sol.
Arsenite . .	None.	None.	Yellow ppt.	Sol.
Arsenate . .	None.	None.	Brown ppt.	•
Carbonate . .	$CO_2\uparrow.$	•	White ppt.	Sol.
Cyanide . .	$HCN\uparrow.$	•	White ppt.	Insol.
Thiocyanate .	None.	$COS\uparrow S\downarrow.$	White ppt.	Insol.
Silicate . .	White ppt. ?	•	Yellow ppt.	Sol.
Borate . .	None.	None.	White ppt.	Sol.
Ferrocyanide .	None.	$CO\uparrow.$	White ppt.	Insol.
Ferricyanide .	None.	$CO\uparrow.$	Orange ppt.	Insol.
Normal oxide ²	None.	None.	•	•
Peroxide ² .	None.	$Cl_2\uparrow.$	•	•
Metal ². .	None.	$H_2\uparrow.$	•	•

NOTES

• DO NOT TRY THIS TEST.

¹ Orthophosphate. For other phosphates see p. 236.

² These are not anions, but are conveniently listed here because of their reactions with the general reagents.

³ Due to chloride present as impurity.

⁴ Goes yellow, brown and black on standing.

10, 7   CATIONS OF GROUP 1

Analytical Group 1 includes silver Ag^+, lead Pb^{++}, and mercurous Hg_2^{++} ions. These ions are precipitated as their chlorides, which are all white.

SPECIAL TEST

To the solution containing the chloride precipitate from the group test, add dilute ammonia. Results are as follows :

Precipitate " dissolves "	.	.	.	.	Silver.
Precipitate remains white	.	.	.	.	Lead.
Precipitate becomes black	.	.	.	.	Mercurous.

CONFIRMATORY TESTS

Cation	Tests	For details see pp.
Silver .	Hydroxide,[5] iodide, chromate, charcoal block	194-195
Lead .	Iodide, chromate, sulphate, hydroxide, charcoal block	225-226
Mercurous .	Iodide, hydroxide	207

[1] A white or pale yellow precipitate of sulphur may be formed here by the oxidation of hydrogen sulphide by nitric acid, ferric salts, dichromates or permanganates.

[2] Ferrous hydroxide is soluble in ammonium chloride solution and the ferrous ion is, strictly speaking, in Group 4. Ferrous salts are, however, nearly always contaminated with ferric salts, which are precipitated in Group 3. It is therefore customary in analysis to oxidise ferrous salts with nitric acid to ferric salts, so that all the iron is precipitated by the Group 3 reagent.

[3] This is to depress the ionisation of ammonium hydroxide and so prevent the precipitation of the less-sparingly soluble hydroxides of metals in Groups 4 and 5, and of magnesium. Some of these metals also form ammonia-complex ions, the hydroxides of which are soluble in water.

[4] If sodium carbonate were used as precipitant here, magnesium would be precipitated as well as calcium, strontium and barium. Ammonium carbonate is hydrolysed in solution thus :

$$2NH_4^+ + CO_3^{--} \;\rightleftharpoons\; 2NH_3 + CO_2 + H_2O,$$
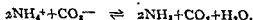
and the extent of hydrolysis is increased by the presence of excess ammonium ions. The concentration of carbonate ions is thus decreased, and magnesium is not precipitated, since its carbonate is more soluble than those of the other three metals.

[5] Ionic precipitation reactions are indicated by the names of the anions to be used.

IDENTIFICATION OF THE CATION

10, 6   THE GROUP SEPARATION

The logical processes involved in this method and their peculiar emphasis on negative evidence have been discussed in chapter 2 (pp. 11-12). Chemically, the classification is based on differences in the solubility of the sulphides, as explained briefly in chapter 6 (pp. 90-91).

Other steps in the classification are explained in footnotes on p. 287.

O.S. (1 ml.)
Add dil. HCl (1 ml.).

No precipitate   **Precipitate**

To above mixture add H₂S water   Group 1.
(5 ml.) or saturate with H₂S gas.   (See p. 287.)

No precipitate   **Precipitate**

To O.S. (2 ml., fresh portion) add   Group 2.[1]
conc. HNO₃ (5 drops), boil and cool[2];   (See pp. 288-
add[3] NH₄Cl soln. (2 ml.) and make   289.)
alkaline with NH₄OH.

No precipitate   **Precipitate**

Divide above mixture into two equal   Group 3.
parts (A and B). To A add H₂S water   (See pp. 289-
(5 ml.) or saturate with H₂S gas.   290.)

No precipitate   **Precipitate**

To B add (NH₄)₂CO₃ soln. (2 ml.).[4]   Group 4.
                                                      (See p. 290.)

No precipitate   **Precipitate**

Group 6.   Group 5.
(See pp. 291-   (See pp. 290-
292.)   291.)

1, 2, 3, 4. See opposite page.

CONFIRMATORY TESTS

Cation	Tests	For details see pp.
Antimony	Sulphide and ammonium polysulphide, sodium hydroxide, charcoal block.	241
Cadmium	Sodium hydroxide, charcoal block.	204
Stannic	Sodium hydroxide, sulphide and ammonium polysulphide, charcoal block.	222, 224
Arsenious	Sodium hydroxide and copper sulphate (reduction), charcoal block.	238
Copper	Colour of O.S. Ammonium hydroxide, iodide, ferrocyanide, charcoal block, borax bead, flame test.	192-193
Mercuric	Iodide, heat.	205-206
Bismuth	Precipitation of basic salt by water. Iodide, charcoal block.	242
Lead	Iodide, chromate, sulphate, charcoal block	225-226
Stannous	Reduction of permanganate or dichromate, sulphide and ammonium polysulphide. Charcoal block.	222-223

10, 9

CATIONS OF GROUP 3

Analytical Group 3 consists of the following cations, which are precipitated as their hydroxides by ammonium hydroxide in the presence of ammonium chloride ; colours of the precipitates are given in brackets :

Ferric Fe^{+++} (brown).   Chromic Cr^{+++} (green).
Aluminium Al^{+++} (white).

SPECIAL TESTS

1. The colour of the hydroxide precipitate distinguishes at once between the three cations.

2. If iron is present (brown hydroxide precipitate) it is necessary to determine whether this was in the ferrous or ferric condition before oxidation with nitric acid.

To O.S. (1 ml.) add potassium ferricyanide (1 ml.).
Dark blue precipitate indicates ferrous iron.
Brown colour   „   ferric iron.

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CATIONS OF GROUP 2

Analytical Group 2 consists of the following cations, which are precipitated as sulphides by hydrogen sulphide in acid solution; the colours of precipitates are given in brackets.

Lead Pb++ (black).   Copper Cu++ (dark brown).
Bismuth Bi+++ (dark brown).   Mercuric Hg++ (black).
Cadmium Cd++ (yellow).   Stannous Sn++ (dark brown).
Stannic Sn++++ (yellow).   Arsenious As+++ (yellow).
Antimony Sb+++ (orange).

In advanced work, where the separation of two or more cations may be necessary, this Group is divided into two Subgroups, viz.: A (sulphides insoluble in ammonium polysulphide) Pb++, Cu++, Bi+++, Hg++, Cd++, and B (sulphides " soluble " in ammonium polysulphide) Sn++, Sn++++, As+++, Sb+++. This division is unnecessary in work with single substances.

SPECIAL TESTS

These tests depend mainly on the characters of the hydroxides of the cations (some are purely basic, others amphoteric).

1. Note the colour of the sulphide precipitate :

Orange   indicates Sb+++.
Yellow   ,,   Cd++, As+++, Sn++++.
Dark brown
  or black   ,,   Pb++, Cu++, Bi+++, Hg++, Sn++.

2. If the sulphide precipitate is *yellow*, distinguish between the three possible cations as follows :

To O.S. (1 ml.) add ammonium hydroxide until no further change occurs.

White precipitate " soluble " in excess indicates cadmium.
White precipitate insoluble in excess   ,,   stannic.
No precipitate   ,,   arsenious.

3. If the sulphide precipitate is *dark brown or black*, distinguish between the five possible cations as follows :

To O.S. (1 ml.) add sodium hydroxide until no further change occurs.
Blue precipitate   .   indicates cupric.
Yellow precipitate   ,,   mercuric.
White precipitate insoluble in excess   ,,   bismuth.
White precipitate soluble in excess   ,,   lead, stannous (see
                                              4 below).

4. Lead and stannous ions may be distinguished as follows :
To O.S. (1 ml.) add dilute sulphuric acid (1 ml.):
White precipitate indicates lead.
No precipitate   ,,   stannous.

SPECIAL TESTS

The three cations may be distinguished most simply by their flame colours, which are as follows :

Orange red	.	.	.	.	.	Calcium.
Crimson	.	.	.	.	.	Strontium.
Pale green	.	.	.	.	.	Barium.

CONFIRMATORY TESTS

Test	Calcium	Strontium	Barium
Potassium chromate and acetic acid.	No ppt.	No ppt.	Ppt.
Calcium sulphate (boiling) .	No ppt.	Ppt.	Ppt.
Ammonium oxalate . .	Ppt.	Ppt.	Ppt.
Sodium phosphate . .	Ppt.	Ppt.	Ppt.

For details see pp. 198-201.

10, 12   **CATIONS OF GROUP 6**

Analytical Group 6 consists of five cations (magnesium Mg^{++}, ammonium NH_4^+, potassium K^+, sodium Na^+, hydrogen H^+), which are *not* precipitated by any of the previous group reagents.

SPECIAL TESTS

1. Take O.S. (1 ml.), make alkaline with sodium hydroxide solution; if no precipitate appears, boil.

      White precipitate   indicates magnesium.

      Evolution of ammonia   ,,   ammonium.

2. If no positive result has been obtained in test 1, do the flame test on the "unknown" moistened with hydrochloric acid, observing the flame with the naked eye, and through cobalt blue glass (see p. 190).

Flame reddish-purple when seen through blue glass . . } indicates potassium.

Flame almost invisible through blue glass, *strong* orange colour when seen with naked eye . } ,, sodium.

No flame colour, or faint orange colour, when seen with the naked eye . . . } ,, absence of sodium and potassium (see 3).

3. If all the above cations have been proved absent, and the "unknown" or its solution in water is strongly *acid* to litmus, the cation is *hydrogen*, i.e., the original substance is an acid.

CONFIRMATORY TESTS

Cation		Tests	For details see pp.
Ferrous	.	Colour of O.S. Sulphide, ferrocyanide, reduction of permanganate or dichromate, borax bead . . .	270-271
Ferric .	.	Colour of O.S. Thiocyanate, ferrocyanide, oxidation of iodide, borax bead .	270-272
Chromium	.	Colour of O.S. Sodium hydroxide, oxidation to chromate, charcoal block, borax bead	256
Aluminium	.	Sodium hydroxide.	211

10, 10   **CATIONS OF GROUP 4**

Analytical Group 4 consists of the undermentioned cations which are precipitated as sulphides by ammonium sulphide. The colours of the cations (*i.e.*, of the salts in aqueous solution) and of the sulphides, which are given in the following table, are sufficient to identify each cation in elementary work:

Cation			Colour of Ion	Colour of Sulphide
Zinc, Zn^{++} .	.	.	Colourless.	White.
Manganese, Mn^{++}	.	.	Very pale pink.	Pink.
Nickel, Ni^{++} .	.	.	Green.	Black.
Cobalt, Co^{++} .	.	.	Pink.	Black.

CONFIRMATORY TESTS

Cation		Tests	For details see pp.
Zinc	.	Sodium hydroxide, charcoal block .	202-203
Manganese	.	Sodium hydroxide, oxidation to permanganate, borax bead . . .	268-269
Nickel .	.	Sodium hydroxide, ammonium hydroxide, borax bead	276
Cobalt .	.	Sodium hydroxide, ammonium hydroxide, formation of cobaltinitrite, borax bead .	275

10, 11   **CATIONS OF GROUP 5**

Analytical Group 5 consists of three cations (calcium Ca^{++}, strontium Sr^{++}, barium Ba^{++}) precipitated by ammonium carbonate as their carbonates, all of which are white.

The following tests may identify the substances, or may suggest further lines of attack :

a. Appearance.

b. Behaviour on heating alone.

c. Behaviour on heating with sodium carbonate on the charcoal block.

d. Borax bead test.

e. Behaviour with aqua regia (the sulphides will " dissolve ").

f. Treatment with boiling saturated sodium carbonate solution, giving solutions for anion and cation testing (see p. 216).

FURTHER READING

BREWER, F. M. Elementary Qualitative Analysis. Clarendon Press, Oxford, 1933.

VOGEL, A. I. A Text-Book of Qualitative Chemical Analysis, 3rd edition. Longmans, Green, London, 1945.

TREADWELL, F. P. Analytical Chemistry, vol. I., Qualitative Analysis, 9th English edition, translated and revised by HALL, W. T. Wiley, New York, 1937.

CONFIRMATORY TESTS

Cation	Tests	For details see pp.
Magnesium .	Phosphate, sodium carbonate . . .	197
Ammonium .	Nessler's test. Heat. Cobaltinitrite, acid tartrate	228-229
Potassium .	Cobaltinitrite, perchlorate, acid tartrate .	191
Sodium .	Antimonate (ppt.), cobaltinitrite or perchlorate or acid tartrate (no ppt.) . .	190
Hydrogen .	Sodium carbonate	188

10, 13   MISCELLANEOUS SUBSTANCES

The introduction of insoluble phosphates and of substances which dissolve neither in water nor in dilute acids complicates an already rather elaborate identification scheme. In the author's opinion this complication is undesirable.

Some users of this book may wish to include such substances—perhaps asking students to " examine and report on the nature of X " rather than to " identify X."

The following notes may be useful:

1. A substance insoluble in water but " soluble " in dilute acid gives a white precipitate in Group 3, but does *not* give the confirmatory tests for aluminium.

Test a nitric acid solution of the substance for phosphate by the molybdate test. If the result is positive, carry out the flame test. If this test indicates calcium, strontium or barium, the substance is identified. If no flame colour is obtained, bring the phosphate into solution by a sodium carbonate extraction (see p. 216) and identify the cation in the usual way.

2. A substance is insoluble in water, dilute hydrochloric acid and dilute nitric acid.

Such substances are:

(i) water-insoluble salts of strong acids (silver halides; mercurous chloride, mercuric iodide; lead, barium and strontium sulphates);
(ii) sulphides of some metals in Analytical Groups 1 and 2;
(iii) some oxides (of aluminium, chromium, tin, silicon);
(iv) some non-metals (carbon, sulphur, iodine).

Organic Chemistry	Inorganic Chemistry
Compounds containing Carbon	*Compounds not containing Carbon*
3. Reactions are carried out, some without solvent, some in aqueous solution, some in non-aqueous solution. In many re- actions complete absence of water is essential (*i.e.*, all appar- atus and materials must be *dry*).	Reactions are carried out, some without solvent, some in aqueous solution,[1] very few in non-aqueous solution.
4. Most reactions are non- ionic and therefore slow (*e.g.*, hydrolysis of esters).	Many reactions are ionic and therefore instantaneous (*e.g.*, pre- cipitation of insoluble salts).
5. Many compounds are vola- tile at moderate temperatures (o°–300°); compounds are often separated by distillation.	Few compounds are volatile at moderate temperatures; distil- lation is rarely used.[2]
6. Most compounds belong to one or other of a number of well-defined chemical families. The . . . their *chemical properties* that the latter will not serve for the separation of the members from one another or for their identi- fication (see pp. 302 and 359).	There are few families of closely-related inorganic com- pounds, and even in these families differences in chemical and physical properties between the members are usually large enough to make separation or identification easy.
7. Compounds of the same type may or may not show ap- preciable differences from one another in their *physical proper- ties*. Where differences in phy- sical properties are large, these make the separation or identi- fication of the compounds easy. Where differences in physical properties are small, separation or identification of the com- pounds is difficult (see pp. 33–34 and 303).	

[1] Reactions of ions in aqueous solution are over-emphasised in many ele- mentary courses, since these reactions are the most convenient for laboratory work.

[2] Except for the purification of water.

ORGANIC CHEMISTRY

Chapter 11

PRINCIPLES

This chapter outlines the principles of organic chemistry in the broadest possible way. The student is advised to read it only after he has attended some preliminary lectures on organic chemistry introducing him to structural formulæ, and has studied several classes of compounds in lectures and in the laboratory.

11, 1 THE SPECIAL NATURE OF ORGANIC CHEMISTRY

Organic chemistry (the chemistry of carbon and its compounds) differs from inorganic chemistry (the chemistry of all other elements and their compounds) in many respects. The more fundamental differences are treated in lecture courses and in text-books of theory. Certain differences which can be illustrated in an elementary practical course are listed below.

A warning has been given in the preface that in elementary books many generalisations are made, to which there are exceptions. This warning applies with special force to the extremely broad generalisations made below, and the student will realise, from important exceptions to these statements which will be met during his course, that the differences between organic and inorganic compounds are far from clear-cut.

Organic Chemistry	Inorganic Chemistry
Compounds containing Carbon	*Compounds not containing Carbon*
1. Most compounds are *not* ionised.[1]	Many compounds are ionised, and most can be turned into ionised compounds.[2]
2. Many compounds are insoluble in water, and some are decomposed by it. Those insoluble in water are usually soluble in organic liquids. (Many separations depend on differences in solubilities, see pp. 36-37 and 298.)	Many compounds are soluble in water.[2] Most of those insoluble in water are also insoluble in organic solvents.

[1] The few which do ionise are specially important for this reason (see notes on acidic and basic character and salt formation, pp. 309-311).

[2] Reactions of ions in aqueous solution are over-emphasised in many elementary courses, since these reactions are the most convenient for laboratory work.

Organic Chemistry	Inorganic Chemistry
Compounds containing Carbon	*Compounds not containing Carbon*
3. Reactions are carried out, some without solvent, some in aqueous solution, some in non-aqueous solution. In many reactions complete absence of water is essential (*i.e.*, all apparatus and materials must be *dry*).	Reactions are carried out, some without solvent, some in aqueous solution,[1] very few in non-aqueous solution.
4. Most reactions are non-ionic and therefore slow (*e.g.*, hydrolysis of esters).	Many reactions are ionic and therefore instantaneous (*e.g.*, precipitation of insoluble salts).
5. Many compounds are volatile at moderate temperatures (0°-300°); compounds are often separated by distillation.	Few compounds are volatile at moderate temperatures; distillation is rarely used.[2]
6. Most compounds belong to one or other of a number of well-defined *chemical types*. The members of each type often resemble one another so closely in their *chemical properties* that the latter will not serve for the separation of the members from one another or for their identification (see pp. 302 and 359).	There are few families of closely-related inorganic compounds, and even in these families differences in chemical and physical properties between the members are usually large enough to make separation or identification easy.
7. Compounds of the same type may or may not show appreciable differences from one another in their *physical properties*. Where differences in physical properties are large, these make the separation or identification of the compounds easy. Where differences in physical properties are small, separation or identification of the compounds is difficult (see pp. 33-34 and 303).	

[1] Reactions of ions in aqueous solution are over-emphasised in many elementary courses, since these reactions are the most convenient for laboratory work.

[2] Except for the purification of water.

II, 2 CHEMICAL PROPERTIES OF ORGANIC COMPOUNDS

The molecule of every organic compound consists of one or more *hydrocarbon* radicals [1] with or without one or more *substituent* radicals.[1]

The following important radicals are treated in detail in this book.

Hydrocarbon radicals. The alkyl radical, the olefinic double bond, the aromatic nucleus.

Substituent radicals. The hydroxyl, ether, carbonyl, carboxyl, ester, amine, amide, nitro, halogen, sulphonic acid and sulphonamide radicals.

Examples of structural formulæ, showing the way in which radicals are combined, are as follows :

Hydrocarbon radicals thus CH_3-.   Substituent radicals thus $-OH$.

Ethane CH_3-CH_3.

Ethyl alcohol C_2H_5-OH.

Aminoacetic acid $H_2N-CH_2-C\underset{\displaystyle OH}{\overset{\displaystyle O}{\big\langle}}$

Ethyl acetate $CH_3-C\underset{\displaystyle O-C_2H_5}{\overset{\displaystyle O}{\big\langle}}$

In general the hydrocarbon radicals are the more chemically-inert, the substituent radicals the more chemically-active parts of the molecule.

The *chemical properties* of each substituent radical are, generally speaking, *independent* of the nature of the *rest of the molecule.* Thus, for example, the carboxyl radical ($COOH$) has the same general chemical properties (ionisation, formation of salts, esters, acid chlorides, etc.) in all the following compounds :

Formic acid $H.COOH$.   Benzoic acid $C_6H_5.COOH$.

Acetic acid $CH_3.COOH$.   Oxalic acid $COOH.COOH$.

                        Acrylic acid $CH_2:CH.COOH$.

                        Chloroacetic acid $Cl.CH_2.COOH$.

Radicals do sometimes interfere with one another's chemical properties, and in more advanced courses much attention must be paid to the nature and extent of this interference. In an elementary course it can (with one exception, see p. 301) be largely neglected without serious consequences. The principle of the independence of radicals is always, however, the foundation of the organic chemist's thought, and

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[1] The word "group" is often used as a synonym for "radical." The author prefers "radical," since "group" may mean either "a group or class of compounds " or "a group of atoms."

the study of organic chemistry is, therefore, largely the study of the properties of the radicals and especially of the substituent radicals.

In subsequent sections of this chapter (pp. 300–304) each part of the practical organic chemistry covered in this book is considered in the light of the principle of the independence of the radicals. Some reactions chosen to illustrate the principle are described on pp. 304–307. Before these matters are dealt with, attention must be given to physical properties.

11, 3 PHYSICAL PROPERTIES OF ORGANIC COMPOUNDS

Compounds which contain the same substituent radicals and differ only in the size of the hydrocarbon radicals present usually resemble one another closely in their chemical properties; they show, however, differences—often large differences—in their physical properties. Some very broad general trends in physical properties, to which there are many exceptions, are given in Table 11, 3, A.

A series of compounds, which have similar chemical properties and the formulæ of which differ by CH_2 from one member to the next, is called a *homologous series*. An example is the homologous series of saturated monocarboxylic acids, viz. :

$H.COOH$, $CH_3.COOH$, $CH_3.CH_2.COOH$, $CH_3.(CH_2)_2.COOH$, $CH_3.(CH_2)_3.COOH$, etc.

The terms "lower," "middle" and "higher" are applied to members of homologous series approximately as follows :

Lower members : those containing 1–5 carbon atoms.
Middle members :   „   6–11   „
Higher members :   „   12 or more carbon atoms.

Many physical properties vary in a very regular manner during the ascent of a homologous series. Details for some properties are given in Table 11, 3, A. Quantitative data for members of one homologous series (the saturated monocarboxylic acids) are given in Table 11, 3, B.

TABLE 11, 3, A

GENERAL RULES FOR PHYSICAL PROPERTIES

Property	General Trend	Variations in ascent of a homologous series
Melting-point.	Rises with increase in molecular weight and in number of substituent radicals (many exceptions).	Rises (some exceptions). Note the alternation in m.ps of acids containing odd and even numbers of carbon atoms in Table 11, 3, B.

Property	General Trend	Variations in ascent of a homologous series
Boiling-point.	Rises with increase in molecular weight and in number of substituent radicals.	Rises very regularly (usually by 20°-30° for each additional CH_2 group).
Density.	For liquids, depends on the proportion of "heavy" substituent radicals (e.g., halogen, carboxyl, etc.) present.	Liquid members of many series tend towards a density of about 0·8 for C_{16} and higher compounds.
Solubility 1. Covalent solutes in organic solvents.	Like dissolves like. Solubility usually decreases as molecular weight of solute increases.	See general trends.
2. Covalent solutes [1] in water.	Solubility depends on the proportion of water-attractive and water-repellent radicals in the solutes.[2] Compounds containing no water-attractive radicals (hydrocarbons and halogen derivatives) are virtually insoluble in water.	Hydrocarbons and halogen derivatives — all members virtually insoluble. Compounds containing a water-attractive radical (e.g., hydroxyl, carbonyl, carboxyl, amine) — falls (since proportion of water-repellent hydrocarbon radical increases).[3]
3. Ionised solutes [2] in organic solvents.	Solubilities in non-hydroxylic solvents (paraffins, benzene, ether) mostly negligible. Some solubilities in hydroxylic solvents (e.g., ethyl alcohol) moderate.	See general trends.
4. Ionised solutes [2] in water.	Most sodium, potassium, and ammonium salts of organic acids and most halides and sulphates of organic bases are readily soluble. If the proportion of hydrocarbon radicals in the molecule is very large, the salts are colloidal electrolytes. Other salts show very irregular behaviour.	See general trends.

[1] Includes slightly-ionised compounds (weak acids and bases).
[2] Chiefly salts.

dissolve.

TABLE II, 3, B

PHYSICAL PROPERTIES OF MONOCARBOXYLIC ACIDS

The acids are the saturated monocarboxylic acids with unbranched chains, H.COOH, CH₃.COOH, etc.

The following properties are listed:

1. Melting-point (m.p.).
2. Boiling-point (b.p.) (at 760 mm. pressure unless stated otherwise).
3. Density (d) in g. per ml. at 20° (approximate).
4. Solubility (s) in water in g. per 100 ml. at 20° (approximate).

∞ =miscible in all proportions

No. of carbon atoms	1	2	3	4	5	6	7	8	9
m.p.	8	17	−20	−8	−34	−1	−10	17	13
b.p.	101	119	141	163	186	205	223	237	254
d	1·22	1·05	1·01	0·98	0·96	0·95	0·92	0·91	0·91
s in water	∞	∞	∞	∞	3·7	0·97	0·24	0·07	0·03

No. of carbon atoms	10	11	12	13	14	15	16	17	18
m.p.	31	28	44	41	54	52	63	62	70
b.p.	269	212*	225*	236*	248*	257*	268*	277*	287*
d	0·88†		0·88†		0·86†		0·85†		0·85†
s in water	0·015	0·009	0·006	0·003	0·0020	0·0012	0·0007	0·0004	0·0003

* At 100 mm. pressure.   † At m.p.

Two other properties remain to be mentioned, viz.: smell and colour. *Smell*, which is often considered as a physical property, is in fact a chemical property, and particular types of smell are associated with particular radicals (*e.g.*, many esters have a "fruity," many aliphatic amines have a "fishy" smell). In a homologous series the intensity of the smell often decreases as the molecular weight increases, due to decrease in volatility. *Colour* is generally associated with particular radicals or combinations of radicals (*e.g.*, the azo radical or quinonoid systems). It is thus allied to the chemical properties.

II, 4   THE GRAMMAR OF ORGANIC CHEMISTRY

The chemistry of the hydrocarbons and of compounds containing a single substituent radical may be called the " grammar " of organic chemistry.

A knowledge of the chemistry of the radicals, gained from the study of such simple compounds, and an understanding of the principle of the independence of radicals enable the student to deduce with fair certainty the reactions of more complex compounds, *i.e.*, to interpret structural formulæ for himself. For example, the compound whose formula is

$$HOCH_2-\overset{\displaystyle NH_2}{\underset{\displaystyle |}{CH}}-COOH,$$
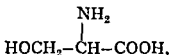
and which contains the substituent radicals —OH, —NH$_2$ and —COOH, undergoes the reactions of these three radicals as expected. It forms, *e.g.*, a benzoyl ester (with the OH radical), a hydrochloride (with the NH$_2$ radical), and a copper salt (with the COOH radical).

There are, indeed, cases where radicals interfere with one another's chemical properties, but with one important exception (see p. 301), these are incidental to the general picture. The chemistry of complex organic compounds cannot be understood without a previous knowledge of the " grammar," and since most organic compounds of bio-logical interest are complex the medical student must have a thorough

. . . . r " of organic chemistry. All reactions described in this chapter are general; reactions peculiar to individual compounds and reactions of compounds containing two or more substituent radicals have been rigorously excluded. Most re-actions are to be carried out as test-tube experiments, but a few large-scale experiments are included, to give the student practice in handling the apparatus used for organic preparations. The student must continually remind himself that all these reactions are *general* reactions of the radicals. If when carrying out reactions with, *e.g.*, acetic acid, he thinks of them simply as reactions of acetic acid, his time is largely wasted. If, however, he thinks of them as general reactions of car-boxylic acids, and is prepared to apply what he learns to the study of more complex compounds, he will find the time well spent.

Special attention is paid to the water-attractive or water-repellent character and to the acidic or basic character (if any) of each radical. These characters are of the utmost importance to students of biology —the first, because water constitutes the greater part by weight of most cells, and therefore the extent to which compounds dissolve in . . . . the second, ... acidity or . . . . great im-portance to the chemist in the detection and separation of different classes of organic compounds (see pp. 309-311 and Chapter 13, pp. 359-374).

11, 5   **AROMATIC COMPOUNDS**

Organic compounds may be divided into three main classes, viz. :

1. *Acyclic.* Compounds in which there are no rings of atoms (also called aliphatic compounds).

2. *Carbocyclic.* Compounds in which there are rings consisting entirely of carbon atoms.

3. *Heterocyclic.* Compounds in which there are rings consisting of carbon and other atoms (O, S, N, etc.).[1]

Among the carbocyclic compounds are many (*e.g.*, benzene C_6H_6) which contain a far smaller proportion of hydrogen than the corresponding acyclic compounds (*e.g.*, hexane C_6H_{11}) but do not behave like highly unsaturated compounds.

These hydrocarbons and their substitution-products, all of which show this unexpectedly " saturated " behaviour, are called *aromatic*. The simplest of the hydrocarbons is benzene, which is commonly represented as
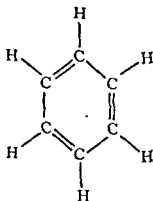
or

Another is naphthalene.
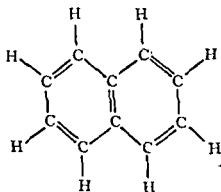
or

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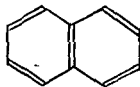
[1] The systematic chemistry of heterocyclic compounds is not considered here, but some compounds of biological importance are treated in Chapter 14. Many heterocyclic compounds show aromatic behaviour.

The rings of carbon atoms with alternate double and single links are called aromatic *nuclei*. The monovalent radical C_6H_5— (benzene minus one hydrogen atom) and similar radicals are called *aryl* radicals.

Aromatic nuclei have some chemical properties of their own, which are not shared by the acyclic hydrocarbon radicals (alkyl radicals).

(This is the one really important case of interference by radicals in one another's properties which the elementary student need consider.)

Other substituent radicals show the same properties, no matter whether *they are attached to an alkyl radical or to an aromatic* nucleus. All substituent radicals if attached to an aromatic nucleus through an alkyl *side-chain* have the *same* properties as in the aliphatic series.

Certain carbocyclic compounds (*e.g.*, cyclohexane C_6H_{12} and its derivatives) show no aromatic behaviour, but resemble acyclic compounds in all respects.

In most lecture courses all aliphatic compounds are dealt with before the aromatic compounds are introduced. This is done because it avoids introducing the difficult idea of the aromatic nucleus at the start. It has the disadvantage that the differences between aromatic and aliphatic compounds are over-emphasised, although, as may be seen from the above, similarities are far more common than differences. The opposite course of introducing aromatic compounds at the start, which will be followed here, avoids this over-emphasis on differences. There is, further, the practical advantage in that some aromatic compounds are cheaper and easier to work with than the corresponding aliphatic compounds.

II, 6   CLASSIFICATION AND IDENTIFICATION OF ORGANIC COMPOUNDS

The identification of a single organic compound is a very different matter from the identification of a single inorganic substance. Nearly all inorganic substances can be turned into ions of some sort in aqueous solution, and these can then be identified by a relatively simple and fool-proof scheme of analysis. On the other hand, few organic compounds can be turned into ions; each substance must be identified as a whole. In addition to chemical tests, quantitative determinations of physical properties and comparison with known substances are nearly always necessary for the complete identification of an organic substance.

The complete identification of a single organic compound consists usually of two distinct parts, the first *chemical*, the second *physical*.

Since the reactions of each substituent radical in an organic com-

pound are largely independent of the nature of the rest of the molecule, *chemical evidence* usually indicates merely what substituent radical or radicals are present in an unknown substance, *i.e.*, to what *class* of compound (alcohol, ketone, amide, etc.) it belongs.

The first part of the process of identification consists, therefore, of a number of general chemical tests which tell the analyst with some certainty to what class of compound the unknown substance belongs. The indications given by each particular test are rarely as clear-cut as the information given by an ionic reaction in inorganic analysis.

The behaviour of the unknown substance with all reagents likely to give information of value must be examined and the results compared with those given by known substances, before a final conclusion is drawn. The argument runs on the following lines, *e.g.*, " The compound shows the same general reactions as ethyl alcohol. It therefore contains a hydroxyl group." Classification thus involves the systematic application of a general knowledge of organic chemistry in the light of the principle of the independence of radicals, and not a series of rule-of-thumb tests.

While members of the same class of organic compounds show little difference from one another in their chemical properties, they show differences, often great, in their physical properties (melting-point, boiling-point, density, refractive index, optical activity, etc.). In the second stage of the identification of an unknown organic substance the analyst determines which *member* of a particular class the substance is, principally by determinations of *physical properties*, either of the compound itself or of its derivatives.

Among these properties the *melting-point* is of supreme importance because of the mixed melting-point method, by which the identity or non-identity of two apparently identical samples may be decided. Nearly every identification depends on the determination of one or more mixed me'*---* ---*--- '*-- -- - --- -- '* -- --* '* 'hough the mixed melting-   melting-point is not suf   *---*mpound, and melting-point determination is obviously impossible in the case of a liquid. Organic chemists have therefore devised reagents which will make solid derivatives from each class of compound. In this book the preparation of some derivatives of carbonyl compounds is described (pp. 330-332), since these are among the easiest derivatives to make.

Chapter 13 of this book outlines a method for the *classification* of organic compounds containing not more than one substituent radical. The classification of unknown compounds provides the student with practice in applying his knowledge of general organic reactions.

This is only the first stage of the full process of identification described above. The second stage of this process—the determination of physical properties of the unknown substance and of its derivatives —is too lengthy to be attempted in an elementary course.

11, 7   ORGANIC COMPOUNDS OF BIOLOGICAL IMPORTANCE

Chapter 14 of this book deals with the pure chemistry of some organic compounds of biological importance. The metabolism of these compounds (*i.e.*, the changes which they undergo in living organisms) is the province of the biochemist, and is not considered here.

The first part of the chapter deals with the fats, carbohydrates and proteins which, together with water, are the chief constituents of all living organisms and the chief foodstuffs of animals.

The latter part of the chapter deals with a wide variety of substances which for one reason or another are of biological importance. Some substances are representative of patterns (*e.g.*, steroids, purines) which are used by nature for many different physiological purposes. Other substances (*e.g.*, formaldehyde, salicylic acid, sulphonamide drugs) are included because they will be encountered in some other branch of medical study.

For each compound or group of compounds, those reactions which are *general reactions* of the substituent radicals are treated first. These reactions cannot be understood without a knowledge of the " grammar " of organic chemistry and an understanding of the principle of the independence of radicals. Special reactions which depend on the presence of a number of radicals are considered after the general reactions. Some of these special reactions are empirical tests, whose *precise mechanism is not understood.*

Where relevant, mention is made of the application of the reactions described in this chapter to the detection and determination of compounds in biological material, including human tissues, body fluids or excreta. The results of such tests often give information of clinical value.

In medical work the tests usually have to be done on urine, faeces, blood or cerebrospinal fluid. While the reactions described in Chapter 14 may be simple, their application in clinical work is often complicated for the following reasons :

1. The substances under examination may be present in very low concentration.

2. Many other substances present may interfere with the tests.

3. The amounts of material available are small (especially when tests have to be made on blood).

Interpretation of the results is often difficult because of the very wide variations in results obtained with healthy persons.

11, 8   EXPERIMENTS ILLUSTRATING INDEPENDENCE OF RADICALS

A. Comparison of Acetic Acid ($CH_3.COOH$) and Heptoic Acid ($CH_3(CH_2)_5.COOH$).

The purpose of this comparison is to show that while members of a homologous series differ in physical properties, they are identical in

many chemical properties since they contain the same substituent radical.

1. Solubility.

Acetic acid, in which the water-attractive carboxyl radical forms a large part of the molecule, is miscible with water in all proportions. Heptoic acid, in which the carboxyl radical is a very small part of the molecule, is almost immiscible with water.

Investigate the miscibility of acetic acid and of heptoic acid with water by the general method for liquids described on p. 312.

2. Melting-Point, Boiling-Point, Density.

Values for these properties, which cannot be measured conveniently by the student, are given on p. 299.

3. Acidity.

Both acetic and heptoic acids ionise slightly thus

$$R.COOH \rightleftharpoons R.COO^- + H^+.$$

Both acids react with bases to form salts. Since both acids are stronger than carbonic acid, they displace the latter from carbonates or bicarbonates. Although heptoic acid is sparingly soluble in water, sodium heptoate is readily soluble. Both acids, being weak, are displaced from their salts by strong mineral acids.

For details of experiments see p. 338, reactions 1 (a), (b) and (c).

4. Esterification.

Both acids may be esterified by alcohols thus :

$$R.COOH + HOR' = R.COOR' + HOH.$$
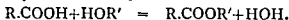
(a) For details of the esterification of acetic acid see p. 323, reaction 1 (c).

(b) Details of the esterification of heptoic acid are as follows : Heat together for 10 minutes in the boiling water bath ethyl alcohol (20 drops), heptoic acid (10 drops) and concentrated sulphuric acid (1 drop). Cool, and neutralise with sodium hydroxide. Ethyl heptoate separates as an oil, the smell of which resembles that of ethyl acetate.

5. Formation of Acid Chlorides.

Both acids on treatment with phosphorus pentachloride yield acid chlorides. $R.COOH + PCl_5 = R.COCl + POCl_3 + HCl\uparrow$.
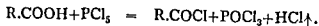
For details of experiments see p. 340, reactions 5 (a) and (b).

B. Reactions of Chloroacetic Acid (Cl.CH₂.COOH)

The purpose of these experiments is to show that, in a compound containing two or more substituent radicals, each radical behaves (in general) in the same way as when it is the only substituent radical in a compound. Thus in chloroacetic acid the chloride radical behaves almost precisely in the same way as the chloride radical in amyl chloride, $Cl.(CH_2)_4.CH_3$, or in benzyl chloride, $Cl.CH_2.C_6H_5$. Similarly the carboxyl radical (COOH) behaves in almost exactly the same way as the carboxyl radical in acetic acid, $CH_3.COOH$.

REACTIONS OF THE CHLORIDE RADICAL [1]

1. Non-Ionic Nature of Chloride.

The chloride radical in chloroacetic acid is covalently-linked to carbon. It therefore does *not* give the reactions of chloride ion.

To chloroacetic acid (1 spatula-point) [2] in water (2 ml.) add silver nitrate solution (5 drops). No precipitate is produced.

2. Hydrolysis of Halide Radical by Alkali.

On boiling chloroacetic acid with excess sodium hydroxide in aqueous solution, hydroxyacetic acid (sodium salt) and sodium chloride are formed.

$$Cl.CH_2.COO^- + OH^- = HO.CH_2.COO^- + Cl^-.$$

The chlorine is now present as chloride ion, and gives a precipitate on the addition of nitric acid and silver nitrate solution.

Boil chloroacetic acid (1 spatula-point) with dilute sodium hydroxide (5 ml.) for two minutes. Cool, acidify with dilute nitric acid and add silver nitrate solution (5 drops). A white precipitate of silver chloride is formed.

REACTIONS OF THE CARBOXYL RADICAL [3]

3. Acidic Properties.

Chloroacetic acid forms salts with bases and displaces weaker acids (*e.g.*, carbonic) from their salts. It is a stronger acid ($pK_a = 2.81$) than acetic acid ($pK_a = 4.75$).

$$Cl.CH_2.COOH + OH^- = Cl.CH_2.COO^- + HOH.$$
$$Cl.CH_2.COOH + HCO_3^- = Cl.CH_2.COO^- + CO_2 + H_2O.$$

(*a*) Take in a porcelain basin bench sodium hydroxide solution (2M, 5 ml.) and add chloroacetic acid (2M aqueous solution) until the solution is just acidic to phenolphthalein paper. Evaporate the solution to dryness on the boiling water bath. Sodium chloroacetate is left as a white crystalline solid.

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[1] Compare pp. 353-354.
[2] This arbitrary measure for solids is illustrated on p. 443.
[3] Compare pp. 336-340.

(b) To chloroacetic acid (1 spatula-point) in water (2 ml.) add sodium bicarbonate solution (2 ml.). Effervescence occurs, carbon dioxide being evolved.

4. Esterification.

The carboxyl radical of chloroacetic acid can be esterified exactly like that of acetic acid.

$$Cl.CH_2.COOH + HO.C_2H_5 = Cl.CH_2.COO.C_2H_5 + HOH.$$

Heat together in a boiling water bath for two minutes chloro-acetic acid (4 spatula-points), ethyl alcohol (2 ml.), concentrated sulphuric acid (1 drop). Cool, add dilute sodium hydroxide dropwise until the mixture is just alkaline to litmus. Ethyl-chloroacetate (characteristic ester smell) separates as a lower layer.

5. Reaction with Phosphorus Pentachloride.

The carboxyl radical forms an acid chloride as does the carboxyl radical of acetic acid.

$$Cl.CH_2.COOH + PCl_5 = Cl.CH_2.COCl + POCl_3 + HCl\uparrow.$$

(Fume Cupboard.) Mix in an ignition-tube phosphorus penta-chloride and chloroacetic acid (¼ spatula-point each) and warm gently. A vigorous reaction occurs, hydrogen chloride being evolved.

FURTHER READING

This list of books for further reading covers Chapters 11, 12 and 13.

ELEMENTARY THEORETICAL TEXT-BOOKS

HOLMYARD, E. J. Outlines of Organic Chemistry, 2nd edition. Arnold, London, 1936.

READ, J. An Introduction to Organic Chemistry (8th Impression). Bell, London, 1945.

READ, J. A Text-Book of Organic Chemistry. Bell, London, 1932. (Larger than the preceding reference.)

Any of these text-books is suitable for a first-year medical course.

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COHEN, J. B. Practical Organic Chemistry, 3rd edition. Macmillan, London, 1926. (Useful for preparations.)

ROBERTSON, G. R. Laboratory Practice of Organic Chemistry, Revised edition. Macmillan, New York, 1943. (Includes a good short treatment of the theoretical principles on which practical methods—e.g., distillation, crystallisation—are based.)

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ROBERTSON, G. R. Laboratory Practice of Organic Chemistry, Revised edition. Macmillan, New York, 1943.

(Includes a good short treatment of the theoretical principles on which practical methods—e.g., distillation, crystallisation—are based.)

CLARKE, H. T. A Handbook of Organic Analysis, 4th edition. Arnold, London, 1931.

CAMPBELL, N. Qualitative Organic Chemistry. Macmillan, London, 1939.

>(The last two books deal chiefly with the identification of the simpler organic compounds, and thus extend Chapter 13 of this book.)

PROBLEMS

SMITH, J. L. B. and RINDL, M. Numerical and Constitutional Exercises in Organic Chemistry. Methuen, London, 1941.

>(Provides excellent practice in the application of the principles of organic chemistry to the solution of constitutional problems.)

LARGER TEXT-BOOKS

HICKINBOTTOM, W. J. Reactions of Organic Compounds. Longmans, Green, London, 1936.

>(An excellent single volume work which treats organic chemistry as the study of the reactions of radicals. Gives full details of many preparations and numerous references to the literature.)

SCHMIDT, J. A Text-Book of Organic Chemistry, 5th English edition by CAMPBELL, N. Gurney and Jackson, Edinburgh, 1946.

KARRER, P. Organic Chemistry (translated into English by MEE, A. J.). Elsevier, Amsterdam, 1938.

GILMAN, H. Organic Chemistry: An Advanced Treatise, 2nd edition, 2 vols. Wiley, New York, 1943.

>(Deals very thoroughly with some selected topics, e.g., carbohydrates, steroids, porphyrins.)

If a student wishes to pursue the subject further, he should ask a senior worker to help him to use the many monographs available on special topics, the great works of reference, and the original literature.

Organic chemistry is very well provided with exhaustive works of reference, among which BEILSTEIN'S *Handbuch der Organischen Chemie* and the Indexes of Abstracts (German, American and British) are of paramount importance. BEILSTEIN summarises all the information available up to 1919 about every organic compound then known, and gives references to the original literature. The Abstract Indexes enable the worker to locate quickly all information about any compound published since 1919.

REACTIONS OF ORGANIC RADICALS

INTRODUCTION

This chapter deals with the "grammar" of organic chemistry. *i.e.*, the properties of hydrocarbon radicals and substituent radicals. These properties are illustrated by hydrocarbons and by simple compounds each containing only one substituent radical. The section for each radical is arranged as follows.

GENERAL DESCRIPTION

The formulæ and names of the radical and of the classes of compounds containing it are given.

The following symbols are used in formulæ and equations :

R=any alkyl or aryl radical.
Alk=any alkyl radical.
Ar=any aryl radical.
Hal=a halogen (Cl, Br, I).

Cases where the attachment of a substituent radical to an aromatic nucleus alters the properties of the former are specially noted.

Solubility in Water.

Hydrocarbon radicals. These are all strongly water-repellent and all hydrocarbons are therefore virtually insoluble in water.

Substituent radicals. The extent to which the radical is water-attractive is noted. T'   ·   ·'   ·.   ' f   .   . ·.·· ,
and the rules about   ·   ·   · : ,
will enable the stude
other members of the same homologous series.   ·

Acidic or Basic Character. Salt Formation.

Hydrocarbon radicals. No hydrocarbon radical has acidic or basic character. All hydrocarbons are therefore *neutral* substances.

Substituent radicals. The acidic or basic character (if any) of each radical is noted. All substituent radicals considered here are neutral *except* carboxyl, sulphonic acid, hydroxyl (in phenols) and sulphon-amide radicals which are *acidic* (*i.e.*, give rise to hydrogen ions) and amine radicals which are *basic* (*i.e.*, give rise to hydroxyl ions).

The acidic or basic character of these radicals provides a means of distinguishing and separating substances containing them from neutral substances. Acidic or basic organic compounds can be *dis-*

309

tinguished from neutral compounds by their action on indicators, or by the methods for separation which are described below.

The *separation* of acidic or basic from neutral compounds frequently depends on salt formation and upon changes in solubility as a result of this. Most organic acids or bases are *weak* electrolytes, *i.e.*, they are only slightly ionised in aqueous solutions, and they are wholly unionised when pure or when dissolved in non-ionising solvents. Benzoic acid, for example, is slightly ionised in aqueous solution thus

$$C_6H_5.COOH \quad \rightleftharpoons \quad C_6H_5.COO^- + H^+ ;$$

in the solid state or in ether it is present entirely as unionised molecules $C_6H_5.COOH$. The solubilities of these weak acids and bases in water and in non-hydroxylic solvents depend upon the proportions of water-attractive and water-repellent radicals in their molecules (see p. 298).

The salts formed by weak organic acids and bases with strong inorganic bases and acids respectively (*e.g.*, with sodium hydroxide and hydrochloric acid) are *strong* electrolytes, *i.e.*, they are completely ionised both in aqueous solution and in the pure state. Examples are sodium benzoate ($C_6H_5COO^-Na^+$) and aniline hydrochloride ($C_6H_5NH_3^+Cl^-$). These ionised compounds are as a rule almost insoluble in non-ionising solvents such as ether or benzene. Many of them are readily soluble in water, even if they contain large hydrocarbon radicals which make the parent acids or bases sparingly soluble in water and readily soluble in ether or benzene. Compare[1] the following solubilities at 20°:

Compound	Approximate Solubility (g. per 100 ml.)	
	in water	in ether
Benzoic acid . . .	0·3	40
Sodium benzoate . . .	66	n
Aniline	3	∞
Aniline hydrochloride .	107	n

Neutral compounds are not more soluble in aqueous acid or alkali than in water. A mixture of an acidic substance (HA) and a neutral substance (X), both insoluble in water, can usually be separated as follows. The mixture is treated with aqueous alkali (*e.g.*, sodium hydroxide); HA is transformed into the salt Na^+A^-, which dissolves in the water present; X remains unchanged and may (if solid) be filtered off or (if liquid) be separated or extracted with (*e.g.*) ether. Similarly a mixture of a basic and a neutral substance could be separated by the use of *aqueous acid*. Such separations *depending on salt*

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[1] The student should test the solubilities of these substances in water and ether, using the quantities detailed on pp. 312-313.

formation are among the most clear-cut separations available to the organic chemist.

Much use is made of solubilities in aqueous acid and alkali in the classification of organic compounds (see Chapter 13).

Colour.

No radical discussed here confers visible colour on all compounds containing it. Traces of yellow or brown impurities are often present in compounds which, when pure, are colourless.

Smell.

Smells, which are often typical of a radical, are not described here, since they are largely a matter of personal opinion. The student should smell all representative compounds provided for study in the laboratory.

REPRESENTATIVE COMPOUNDS

Some physical properties of representative compounds to be studied in the laboratory are listed for reference. These should *not* be learnt. They are included so that the student can deduce roughly for himself the physical properties of other members of the same homologous series, using the rules given in the preceding chapter (pp. 297–299). The properties listed are:

1. Melting-point (m.p.).
2. Boiling-point (b.p.) (at 760 mm. pressure unless stated otherwise).
3. Density (d) in g. per ml. at 20° (approximate).
4. Solubility (s) in water, in g. solute per 100 ml. water at 20° (approximate).

∞ = miscible in all proportions
v = very soluble
sl = slightly soluble
v.sl = very slightly soluble
n = solubility negligible

These abbreviations are used only when quantitative data are not available.

If a liquid A is not miscible in all proportions with water, the solubility of *water in A* is usually of the same order as the solubility of *A in water*. Note the following examples:

	Approximate Solubility (g. per 100 ml.)
Ether in water . .	7
Water in ether . .	1·4
Ethyl acetate in water	9
Water in ethyl acetate	3
Benzene in water .	0·08
Water in benzene .	0·2

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[1] The student should test the solubilities of these substances in water and ether, using the quantities detailed on pp. 312-313.

and grind up with a glass rod. If the substance does not dissolve completely, heat gently to boiling and allow to cool slowly. Note all that happens.

Four "spatula-points"[1] represent anything from 0·05 g. to 0·2 g. solid; solids which do not dissolve completely in these conditions probably have solubilities of less than 10 g. per 100 ml.

Behaviour with Litmus.

Test the aqueous solution or suspension of each compound with red and blue litmus paper. Note and record results and conclusions.

Reactions.

Carry these out as detailed. Use the approximate quantities stated here, *not* two or three times as much.

Reports.

A suggested form for reports is given in the following section.

2, 3   **REPORTS**

The following form of report includes everything which the student has found out for himself, but does not include details of experiments which merely confirm what the book says. Any results which are not as expected must be noted, and an explanation obtained (by the student himself or from a demonstrator). Equations for reactions should be given, substituent radicals being written out *in full*, thus, *e.g.*,

$$-C\!\!\begin{array}{c}\nwarrow O\\ \searrow NH_2,\end{array}$$

not $-CONH_2$; these provide useful practice in translating the general equations given in the book into equations for individual compounds.

14 Apr. 1945.

REACTIONS OF THE AMIDE RADICAL

Reference—Klyne, *Practical Chemistry*, pp. 350-351.

Compounds studied—acetamide $CH_3-C\!\!\begin{array}{c}\nwarrow O\\ \searrow NH_2\end{array}$

benzamide $C_6H_5-C\!\!\begin{array}{c}\nwarrow O\\ \searrow NH_2\end{array}$

[1] This arbitrary measure for solids is illustrated on p. 443.

x

REACTIONS

Reactions are described with generalised equations [1] and with experimental details for laboratory work in the following order :

1. Reactions common to *all* compounds containing the radical.

2. Reactions specific for different *sub-classes* of compounds containing the radical.

In each case ionic reactions, if any, are treated first. These are chiefly reactions connected with the acidic or basic properties of certain radicals.

12, 2 GENERAL INSTRUCTIONS FOR LABORATORY WORK

1. *Reading.*

Before each practical class, read the sections of this chapter describing the radicals to be studied.

2. *Experiments to be done and Materials to be used.*

In most courses it is impossible for students to carry out all the reactions given in this book with each representative compound ; instructors should therefore tell students which tests they wish them to do with each substance. The preliminary examination and the tests with water and litmus should be carried out with *all* the representative compounds if possible.

The author's practice is to detail on the blackboard the substances to be used for each test, the total quantities of each substance required, the way in which each substance is to be obtained (*e.g.*, from a dish on the student's bench, from a stock burette or automatic pipette on the common bench) and (where necessary) the order in which tests are to be done.

3. *Preliminary Examination.*

Note and record the state, colour and smell of each representative compound provided.

4. *Solubility in Water.*

Test each representative compound as follows :

Liquids. The miscibility of the liquid with water over the whole range from 100% water to 100% liquid is investigated thus :

In an ignition-tube take water (20 drops) and add slowly the liquid (20 drops), shaking vigorously after every two or three drops. In a second ignition-tube take the liquid (20 drops) and add slowly water (20 drops), shaking vigorously after every two or three drops. Note the stage (if any), during each addition, at which two liquid layers become visible.

Solids. The method described above for a liquid gives a roughly quantitative idea of its miscibility with water. A similar method for a solid would involve much weighing ; the following method should therefore be used to save time :

Add the solid (4 spatula-points) to water (2 ml.) in a test-tube

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[1] Except in a few cases where the equation is too complicated to be given here, or where the chemistry of the reaction is unknown.

The paraffin hydrocarbons are neutral and virtually insoluble in water.

REPRESENTATIVE COMPOUND

Compound	m.p.	b.p.	d (g. per ml.)	s in water (g. per 100 ml.)
n-Pentane . . $CH_3.(CH_2)_3.CH_3$	$-131°$	$36°$	0.63	0.04

Ordinary pentane is probably a mixture of isomers. The first member of the series (methane CH_4) has been considered on pp. 213-214.

REACTIONS

1. Reaction with Halogens.

Halogens *substitute* themselves for one or more hydrogen atoms in a paraffin hydrocarbon *slowly* (more rapidly in sunlight or with a catalyst).

$$Alk.H + Hal_2 = Alk.Hal + H.Hal.$$
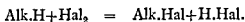
Unsaturated compounds, containing an olefinic double bond, react *rapidly* with the halogens, *adding* two atoms of the latter for each double bond (see p. 316 for comparison of olefin and paraffin hydrocarbons).

2. Inertness towards Permanganate.

Paraffin hydrocarbons do not react with potassium permanganate. Contrast olefins (see p. 317). Alkyl groups attached to an aromatic nucleus are, however, oxidised readily to carboxyl groups by hot permanganate solution.

3. Inertness towards Nitric Acid.

Paraffin hydrocarbons are not nitrated by concentrated nitric acid at ordinary temperature. Contrast aromatic hydrocarbons (see p. 318).

4. Inertness towards Sulphuric Acid.

Paraffin hydrocarbons do not react with and are not dissolved by fuming sulphuric acid at ordinary temperature. Contrast aromatic hydrocarbons (see p. 319).

5. Colour of Iodine Solution.

Solutions of iodine in all hydrocarbons and in their halogen derivatives are *red* or *violet*. Solutions of iodine in all organic compounds containing oxygen or nitrogen are *brown*. This difference is of value in distinguishing hydrocarbons from the ethers, which are rather inert but which contain oxygen (see p. 328 for comparative tests).

Preliminary Experiments.

Test	Acetamide	Benzamide
Appearance.	Colourless crystals.	Colourless crystals.
Smell.	"Mousy."	None.
Solubility in water.	Easily sol. in cold.	Apparently insol. in cold. Sol in hot. Crystallised out on cooling.
Behaviour of solution with litmus.	Red and blue unchanged; substance therefore neutral.	Red and blue unchanged; substance therefore neutral.

Reactions.

The following were carried out; results were as stated in the book except as detailed below.

1. *Hydrolysis with Alkali.*

(a) Acetamide.

$$CH_3-C\overset{\displaystyle O}{\underset{\displaystyle NH_2}{\big<}} \quad +OH^- \quad = \quad CH_3-C\overset{\displaystyle O}{\underset{\displaystyle O^-}{\big<}} \quad +NH_3\uparrow.$$
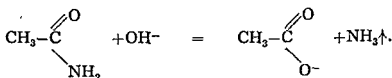
(b) Benzamide.

At first attempt no NH_3 was evolved. Demonstrator suggested that longer heating was necessary; this was tried and proved successful.

$$C_6H_5-C\overset{\displaystyle O}{\underset{\displaystyle NH_2}{\big<}} \quad +OH^- \quad = \quad C_6H_5-C\overset{\displaystyle O}{\underset{\displaystyle O^-}{\big<}} \quad +NH_3\uparrow.$$
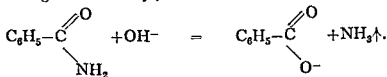
etc., etc.

HYDROCARBON RADICALS

12, 4   THE ALKYL RADICAL

Radical: $C_nH_{2n+1}-$, or Alk−.

Class of compounds: Paraffin or Saturated Hydrocarbons, Alkanes, C_nH_{2n+2} or Alk. H.

Alkyl radicals are usually the least reactive parts of organic molecules containing them, and the paraffin hydrocarbons, which consist entirely of alkyl radicals, are among the least reactive organic compounds. Modern work has shown that the paraffin hydrocarbons are not as inert as was previously thought; most of their reactions cannot, however, be carried out easily in the laboratory.

2. Reaction with Permanganate.

The olefinic double bond reacts rapidly with potassium permanganate (in cold dilute aqueous alkaline solution), giving a dihydroxy-compound (glycol), thus:

$$\text{C=C} \quad +H_2O+ \quad (O) \qquad = \qquad -\overset{|}{\underset{OH}{C}}-\overset{|}{\underset{OH}{C}}-$$

(from $KMnO_4$)
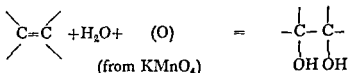
The permanganate is reduced to brown manganese dioxide; the glycol may be oxidised further.

Take pentane, pentene and water (blank test) (2 ml. each) in separate test-tubes. To each tube add bench sodium carbonate solution (5 drops) followed by potassium permanganate (0·1% aqueous solution, 10 drops) and shake. Pentene reduces permanganate, giving a brown colour, pentane does *not* (compare blank test).

3, 4. Reactions with Nitric and Sulphuric Acids.

Olefins react vigorously with the reagents used for the nitration and sulphonation of aromatic compounds, giving complex mixtures of products. These reactions are dangerously violent, and should *not* be attempted here.

12, 6   THE AROMATIC NUCLEUS

Typical nucleus:
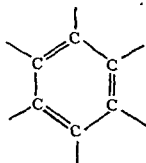
Class of compounds: Aromatic hydrocarbons, Ar.H.

Many hydrocarbons (*e.g.*, benzene, C_6H_6), although containing much less hydrogen than the corresponding paraffins (*e.g.*, hexane, C_6H_{14}), do not behave like highly unsaturated compounds. These hydrocarbons and their substitution-products, all of which show this un-

12, 5   THE OLEFINIC DOUBLE BOND

Radical:

$$\overset{|}{C}=\overset{|}{C}$$

Class of compounds: Olefin Hydrocarbons, Alkenes, C_nH_{2n}.

The olefin hydrocarbons resemble the paraffins in being neutral, and in being virtually insoluble in water.

The principal difference between the olefins and the paraffins is that while the latter are saturated and rather inert, the former are unsaturated and reactive, readily adding two univalent atoms or radicals of various kinds at the double bond.

REPRESENTATIVE COMPOUND

Compound	m.p.	b.p.	d (g. per ml)	s in water (g. per 100 ml.)
1-Pentene $CH_3.(CH_2)_2.CH=CH_2$	$-138°$	$40°$	0·65	n

Ordinary pentene is probably a mixture of isomers; the formula $C_3H_7.CH=CH_2$ may be used in equations. The first member of the series (ethylene, C_2H_4) has been considered on pp. 213–214.

REACTIONS

1. Reactions with Halogens.

The olefinic double bond reacts rapidly with free chlorine or bromine, adding two atoms, thus, *e.g.*:

$$\overset{|}{C}=\overset{|}{C} + Br_2 = \overset{|}{\underset{Br}{C}}-\overset{|}{\underset{Br}{C}}-$$
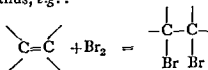
Iodine dissolves in unsaturated hydrocarbons to give a pink solution; the colour fades on standing, since the iodine reacts slowly with the double bond as indicated above for chlorine and bromine (see p. 328).

Take pentane,[1] pentene [1] and carbon tetrachloride (blank test) (2 ml. each) in separate *dry* test-tubes. To each tube add bromine (0·5% solution in carbon tetrachloride, 10 drops) and shake. Pentene decolorises (*i.e.*, reacts with) the bromine; pentane does *not* (compare blank test).

[1] These compounds are both very inflammable; when working with them turn out all naked flames in the vicinity.

The reagent commonly used for nitration is a mixture of concentrated nitric acid and concentrated sulphuric acid. The latter acts as a dehydrating agent, removing water originally present in the nitric acid (about 30% in the ordinary concentrated acid) or produced during the reaction, and as a solvent for the aromatic compound.

The number of nitro radicals introduced in these reactions depends on the temperature and proportions of reagents used.

(a) Nitration of Benzene.

Add concentrated sulphuric acid (2 ml.) slowly with shaking and cooling under the tap to concentrated nitric acid (2 ml.) in a boiling-tube. Then add benzene (20 drops), shaking and cooling as before. The mixture becomes warm and turns yellow in colour. Shake for a minute and pour into another boiling-tube half-full of water. Nitrobenzene separates as a pale yellow oil, denser than water (smell).

Shake up the nitrobenzene with the aqueous liquid, pour 2 ml. of the mixture into another tube and make alkaline with concentrated ammonia. The mixture changes colour from pale yellow to deep orange-yellow due to the formation of salts by traces of polynitro compounds present.

(b) Nitration of Nitrobenzene.

Mix concentrated sulphuric acid (2 ml.), concentrated nitric acid (2 ml.) and nitrobenzene (1 ml.) with shaking and cooling as in (a) above.

Heat the mixture in the boiling water bath for 20 minutes with occasional shaking, cool it thoroughly under the tap and pour it into water (50 ml.). Filter the yellow precipitate of m-dinitrobenzene by suction, recrystallise it from ethyl alcohol and determine the melting-point of the product (m.p. of m-dinitrobenzene is 90°).

(c) Resistance of Paraffins to Nitration.

Repeat (a), using pentane (20 drops) instead of benzene. The mixture does not become warm and remains colourless. On pouring into water pentane separates unchanged (smell).

Note. Many aliphatic compounds other than paraffins react very violently with concentrated nitric acid. Do *not* try to nitrate any unknown substance without finding out from a demonstrator that it is safe to do so.

2. Sulphonation.

Concentrated or fuming sulphuric acid replaces hydrogen atoms in the aromatic nucleus by sulphonic acid ($-SO_3H$ or $-SO_2.OH$) radicals.

$$Ar.H + HO.SO_2.OH = Ar.SO_2.OH + HOH.$$

expectedly " saturated " behaviour, are called *aromatic*. The simplest of the hydrocarbons is benzene, which is commonly represented as:

or

The monovalent radical C_6H_5- (benzene minus one hydrogen atom) and similar radicals are called *aryl* radicals.

The hydrogen atoms attached to an aromatic nucleus undergo many substitution reactions which those of an alkyl radical do not. These substitution reactions take place both with aromatic hydrocarbons and with aromatic compounds already containing one or more substituent radicals. The nature of any substituent radical already present is one of the factors which determine the number of new substituents introduced, the positions into which these go, and the ease of the reaction.

The aromatic hydrocarbons are neutral and virtually insoluble in water.

REPRESENTATIVE COMPOUNDS

Compound	m.p.	b.p.	d (g. per ml.)	s in water (g. per 100 ml.)
Benzene C_6H_6	5°	80°	0·89	0·08
Toluene $C_6H_5.CH_3$ (methylbenzene)	−95°	111°	0·87	0·05
Naphthalene $C_{10}H_8$	80°	218°	1·15	0·003

REACTIONS

1. Nitration.

Nitric acid replaces one or more hydrogen atoms in the aromatic nucleus by nitro ($-NO_2$) radicals.

$$Ar.H + HO.NO_2 \rightleftharpoons Ar.NO_2 + HOH.$$

Few aliphatic compounds react with nitric acid in this way in laboratory conditions.

The reagent commonly used for nitration is a mixture of concentrated nitric acid and concentrated sulphuric acid. The latter acts as a dehydrating agent, removing water originally present in the nitric acid (about 30% in the ordinary concentrated acid) or produced during the reaction, and as a solvent for the aromatic compound.

The number of nitro radicals introduced in these reactions depends on the temperature and proportions of reagents used.

(a) Nitration of Benzene.

Add concentrated sulphuric acid (2 ml.) slowly with shaking and cooling under the tap to concentrated nitric acid (2 ml.) in a boiling-tube. Then add benzene (20 drops), shaking and cooling as before. The mixture becomes warm and turns yellow in colour. Shake for a minute and pour into another boiling-tube half-full of water. Nitrobenzene separates as a pale yellow oil, denser than water (smell).

Shake up the nitrobenzene with the aqueous liquid, pour 2 ml. of the mixture into another tube and make alkaline with concentrated ammonia. The mixture changes colour from pale yellow to deep orange-yellow due to the formation of salts by traces of polynitro compounds present.

(b) Nitration of Nitrobenzene.

Mix concentrated sulphuric acid (2 ml.), concentrated nitric acid (2 ml.) and nitrobenzene (1 ml.) with shaking and cooling as in (a) above.

Heat the mixture in the boiling water-bath for 20 minutes with occasion: :   tap and pour it into wat   :   .   .   . te of m-dinitrobenzene by suction, recrystallise it from ethyl alcohol and determine the melting-point of the product (m.p. of m-dinitrobenzene is 90°).

(c) Resistance of Paraffins to Nitration.

Repeat (a), using pentane (20 drops) instead of benzene. The mixture does not become warm and remains colourless. On pouring into water pentane separates unchanged (smell).

Note. Many aliphatic compounds other than paraffins react very violently with concentrated nitric acid. Do *not* try to nitrate any unknown substance without finding out from a demonstrator that it is safe to do so.

2. Sulphonation.

Concentrated or fuming sulphuric acid replaces hydrogen atoms in the aromatic nucleus by sulphonic acid ($-SO_3H$ or $-SO_2.OH$) radicals.

$$Ar.H + HO.SO_2.OH = Ar.SO_2.OH + HOH.$$

The temperature and the concentration of the acid determine the number of sulphonic acid groups introduced. Paraffin hydrocarbons do not react with concentrated or fuming sulphuric acid.

(a) Sulphonation of Benzene.

Take great care not to spill fuming sulphuric acid on yourself, your clothes or your bench.

To fuming sulphuric acid (2 ml.) add benzene (20 drops, in four portions of 5 drops each). After each portion has been added, shake and cool the tube under the tap. After all the benzene has been added shake for a minute. A homogeneous solution is formed. Pour this very cautiously into water (20 ml.) in a beaker. No oily drops float on the water, *i.e.*, no benzene remains unchanged. The main product, benzenesulphonic acid, and excess sulphuric acid dissolve in the water; a trace of by-product (diphenylsulphone $(C_6H_5)_2SO_2$) separates as a white solid. The separation of the benzenesulphonic acid is too lengthy to be carried out here.

(b) Resistance of Paraffins to Sulphonation.

Repeat (a), using pentane (20 drops) instead of benzene. The pentane does not dissolve; when the mixture is poured into water it separates unchanged.

3. Halogenation.

Aromatic hydrocarbons are halogenated in the nucleus rapidly only in the presence of catalysts. If, however, hydroxyl or amine radicals are already attached to the nucleus, hydrogens of the latter are readily replaced by halogen in aqueous solution.

Aromatic hydrocarbons do not decolorise bromine rapidly (contrast olefins, p. 316); they dissolve iodine to give red or violet solutions (contrast ethers, p. 328).

(a) Behaviour of Benzene with Halogens.

To benzene (2 ml.) add bromine (0·5% solution in carbon tetrachloride, 10 drops) and shake. The bromine is decolorised only on long standing.

(b) Halogenation of a Phenol.

To a saturated aqueous solution of phenol (1 ml.) add bromine water (10 ml.) with shaking. A white precipitate of 2:4:6-tribromophenol is formed.

(c) Halogenation of an Amine.

To aniline (5 drops) suspended in water (1 ml.) add bromine water (10 ml.) with shaking. A dirty white precipitate of 2:4:6-tribromoaniline is formed.

SUBSTITUENT RADICALS

THE HYDROXYL RADICAL

12, 7

Radical: –OH.

Classes of compounds: Alcohols, Alk.OH ; Phenols, Ar.OH.

Organic compounds containing the hydroxyl radical are called *alcohols* unless the radical is directly attached to an aromatic nucleus, in which case they are called *phenols*. Alcohols may be classified as primary, secondary and tertiary—general formulæ:

$$R.CH_2OH, \qquad R.CHOH.R', \qquad R'-\overset{\displaystyle R}{\underset{\displaystyle R''}{\overset{|}{\underset{|}{C}}}}-OH,$$
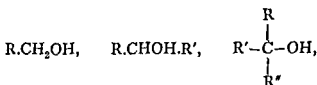
respectively. These three classes of alcohols differ in their behaviour on oxidation (see reaction 8).

The hydroxyl radical is water-attractive. The lowest members of the alcohol series are miscible with water in all proportions ; among the middle and higher alcohols the solubility decreases as the size of the hydrocarbon radical attached to hydroxyl increases. Note that phenol is considerably more soluble in water than *n*-hexyl alcohol.

Phenols are very weak acids, ionising slightly in aqueous solution thus:

$$ArOH \;\; \rightleftharpoons \;\; ArO^- + H^+$$
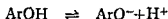
(pK_a for phenol, $C_6H_5.OH$, is 9·89).

Phenols redden litmus if they are sufficiently soluble in water. Alcohols do *not* ionise at all, and therefore have no action on litmus.

Phenols, being acids, react with caustic alkalis to give salts (phenoxides) which are soluble in water.

$$ArOH + OH^- \;\; = \;\; ArO^- + HOH.$$

Whether or not a phenol is soluble in water, it is therefore soluble in aqueous sodium hydroxide. Alcohols do *not* react with alkalis in this way. Since phenols are very weak acids, they are displaced from their salts by any stronger acid (mineral acid, carboxylic acid or even carbonic acid), and if insoluble in water are precipitated:

$$ArO^- + H^+ \;\; \rightleftharpoons \;\; ArOH.$$
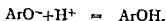
A hydroxyl radical attached to an aromatic nucleus through a side-chain (*e.g.*, in benzyl alcohol, $C_6H_5.CH_2OH$) behaves like the hydroxyl radicals in aliphatic alcohols.

REPRESENTATIVE COMPOUNDS

Compound	m.p.	b.p.	d (g. per ml.)	s in water (g. per 100 ml.)
Alcohols				
Methyl alcohol (methanol) CH_3OH . .	$-98°$	$65°$	0·79	∞
Ethyl alcohol (ethanol) $CH_3.CH_2OH$.	$-117°$	$78°$	0·79	∞
Primary *n*-amyl alcohol (1-pentanol) $CH_3.(CH_2)_3.CH_2OH$.	$-78°$	$138°$	0·82	3
Benzyl alcohol $C_6H_5.CH_2OH$ . .	$-15°$	$205°$	1·05	4
Phenols				
Phenol (hydroxybenzene) $C_6H_5.OH$.	$41°$	$182°$	1·07	7
β-Naphthol (β-hydroxynaphthalene) $C_{10}H_7.OH$ . .	$122°$	$295°$	1·22	0·07

REACTIONS

REACTIONS OF ALL HYDROXY COMPOUNDS

1. Esterification.

All hydroxy compounds react with acid anhydrides or acid chlorides to form esters

$$R-C \begin{matrix} O \\ \\ O \end{matrix} \quad + \quad HOR' \quad = \quad R-C \begin{matrix} O \\ \\ OR' \end{matrix} \quad + RCOOH.$$

$$R-C \begin{matrix} O \\ \\ Cl \end{matrix} \quad + \quad HOR' \quad = \quad R-C \begin{matrix} O \\ \\ OR' \end{matrix} \quad + HCl.$$

(a) Mix ethyl alcohol (1 ml.) and acetic anhydride (1 ml.) in a test-tube and heat in a boiling water bath for 2 minutes. Ethyl acetate is formed. Its smell is masked by those of acetic anhydride and acetic acid, which are removed as follows. Cool, add sodium hydroxide solution dropwise until the mixture is alkaline to litmus. Ethyl acetate (smell) now floats on the top of the aqueous solution.

(b) Repeat (a), using phenol (4 spatula-points) instead of ethyl alcohol. Phenyl acetate is formed. Its smell is not unlike that of phenol, but it is insoluble in sodium hydroxide solution.

Alcohols (but *not* phenols) react with carboxylic acids (usually in presence of concentrated sulphuric acid or dry hydrogen chloride as catalyst) to form esters and water.

$$R-C\overset{\displaystyle O}{\underset{\displaystyle OH}{\diagdown}} +HOR' \rightleftharpoons R-C\overset{\displaystyle O}{\underset{\displaystyle OR'}{\diagdown}} +HOH.$$
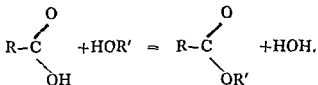
(c) Heat in a test-tube in a boiling water bath for 2 minutes ethyl alcohol (2 ml.), glacial acetic acid (2 ml.) and concentrated sulphuric acid (1 drop). Cool, neutralise excess acetic acid by sodium hydroxide as in (a). Ethyl acetate is formed.

(d) Repeat (c), using benzoic acid (4 spatula-points) instead of acetic acid. Ethyl benzoate is formed (smell).

(e) Preparation of Ethyl Acetate (*LARGE SCALE*).

The reaction is the same as in experiment (c) above. The crude product (i.e., the distillate from the first distillation) contains ethyl acetate, water, ethyl alcohol and acetic acid. The ethyl acetate is purified by the following processes:

1. Sodium carbonate washing—transforms acetic acid into sodium acetate (soluble in water, insoluble in ethyl acetate).

2. Water washings—remove some ethyl alcohol and also any sodium carbonate left behind from the first washing.

3. Treatment with calcium chloride—removes remaining ethyl alcohol and water.

Fit up a distillation apparatus as shown in Fig. 4, 10, A (p. 44). Run into the distilling flask 30 ml. of a mixture of equal volumes of glacial acetic acid and ethyl alcohol, and add concentrated sulphuric acid (10 drops). Distil the mixture very slowly, collecting only that part which distils below 100°.

Transfer the distillate to a separating funnel and add saturated aqueous sodium carbonate solution until the mixture is just alkaline to litmus. Shake thoroughly and allow the mixture to stand for a few minutes. It separates into two layers, the lower being the aqueous layer and the upper the ester layer. Run off the lower

REPRESENTATIVE COMPOUNDS

Compound	m.p.	b.p.	d (g. per ml.)	s in water (g. per 100 ml.)
Alcohols				
Methyl alcohol (methanol) CH_3OH .	$-98°$	$65°$	0·79	∞
Ethyl alcohol (ethanol) $CH_3.CH_2OH$.	$-117°$	$78°$	0·79	∞
Primary *n*-amyl alcohol (1-pentanol) $CH_3.(CH_2)_3.CH_2OH$	$-78°$	$138°$	0·82	3
Benzyl alcohol $C_6H_5.CH_2OH$.	$-15°$	$205°$	1·05	4
Phenols				
Phenol (hydroxybenzene) $C_6H_5.OH$.	$41°$	$182°$	1·07	7
β-Naphthol (β-hydroxynaphthalene) $C_{10}H_7.OH$ . .	$122°$	$295°$	1·22	0·07

REACTIONS

REACTIONS OF ALL HYDROXY COMPOUNDS

1. Esterification.

All hydroxy compounds react with acid anhydrides or acid chlorides to form esters

hydroxide solution; II, sodium bicarbonate solution; III, water (5 drops each). A clear solution of sodium phenoxide is formed in I. In II and III the phenol remains undissolved. To I add dilute hydrochloric acid (5 drops) or pass in carbon dioxide; phenol separates as an oil.

(*b*) Take amyl alcohol (3 drops) in each of two test-tubes. To the tubes add respectively sodium hydroxide solution and water (20 drops). The alcohol is *not* more soluble in sodium hydroxide solution than in water.

5. Colours with Ferric Chloride.

Most phenols give with ferric chloride in aqueous or alcoholic solution characteristic colours (blue, green or purple) due to the formation of co-ordination compounds. Alcohols give *no* colours.

Note that compounds containing some combinations of other radicals (*e.g.*, β-keto-esters) also give coloured co-ordination compounds with ferric chloride.

(*a*) Dissolve phenol (⅓ spatula-point) in water (2 ml.) and add ferric chloride solution (1 drop). A violet colour is produced.

(*b*) Repeat (*a*), using ethyl alcohol (2 drops) instead of phenol. No colour is produced.

6. Millon's Reagent.

Phenols give with Millon's reagent (an aqueous solution of mercurous nitrate, mercuric nitrate and nitric acid) a red colour. Alcohols give *no* colour. The nature of the red product is unknown.

(*a*) Dissolve phenol (₁⁄₁₀ spatula-point) in water (2 ml.). Add Millon's reagent (2 ml.) and heat in a boiling water bath for 30 seconds. A red colour is produced. (Concentrated solutions of phenols give a colour in the cold.)

(*b*) Repeat (*a*), using ethyl alcohol (2 drops) instead of phenol. No colour is produced.

7. Coupling with Diazonium Salts.

Phenols couple with diazonium salts (ArN_2Cl) giving orange or red azo dyes (ArN_2Ar'). Alcohols do *not* react with diazonium salts. The diazonium salts are prepared from aromatic primary amines and nitrous acid. For details, see p. 348.

8. Oxidation by Chromic Acid.

Primary and secondary alcohols are readily oxidised by aqueous potassium dichromate and sulphuric acid to the corresponding carbonyl

layer and discard it. Wash the ethyl acetate in the separating funnel by shaking it with water (three separate 5 ml. portions), discarding the aqueous layers as before. Run the ethyl acetate into a clean, dry boiling-tube, add anhydrous calcium chloride (sufficient to fill the hemispherical part of the tube), cork and label the tube, and " ·: · : ' · ' ' · ﬞ D ·l ﬞ dried product through a sir   ·   ·   ,   ·   and distil it. The fraction ·   .   · ·   · ·   . hyl acetate.

2. Reaction with Metals.

All hydroxy compounds react with the alkali metals, giving compounds of the type RONa (alkoxides or phenoxides), hydrogen being evolved.

$$2ROH + 2Na \;\rightleftharpoons\; 2RO^-Na^+ + H_2\uparrow$$

The alkoxides are decomposed by water, giving the alcohol and sodium hydroxide.

$$RO^-Na^+ + HOH \;\rightleftharpoons\; ROH + Na^+ + OH^-$$

The phenoxides dissolve in water unchanged (compare reaction 4).

(a) To ethyl alcohol (2 ml.) in a porcelain basin add sodium wire (1 inch). Effervescence occurs. When it has ceased, evaporate the solution to dryness on the boiling water bath; a white solid (sodium ethoxide) is formed.

(b) Repeat (a), using a solution of phenol (4 spatula-points) in dry ether[1] (2 ml.) instead of ethyl alcohol. Sodium phenoxide (sodium phenate) is produced. (Ether itself does not react with sodium, see p. 328.)

3. Reaction with Phosphorus Pentachloride.

All hydroxy compounds react with phosphorus pentachloride to give the corresponding chloro compounds, phosphorus oxychloride · : · :·,· ,   ·   ·   · : ·: · :   ·   ·) This · ·   : : ·   ,   ·   · ' . :   ·   :   ·   esters.

$$R.OH + PCl_5 \;=\; R.Cl + POCl_3 + HCl\uparrow.$$

(Fume Cupboard.) To phosphorus pentachloride ($\frac{1}{2}$ spatula-point) add ethyl alcohol (5 drops). A vigorous reaction occurs, fumes of hydrogen chloride being evolved.

REACTIONS WHICH DISTINGUISH BETWEEN ALCOHOLS AND PHENOLS

4. Acidic Properties of Phenols.

For explanation of reactions see the introduction to this section.

(a) Take phenol (2 spatula-points) in each of three test-tubes (I, II and III). To the tubes add the following reagents: I, sodium

[1] Very inflammable. Keep away from naked flames.

hydroxide solution; II, sodium bicarbonate solution; III, water (5 drops each). A clear solution of sodium phenoxide is formed in I. In II and III the phenol remains undissolved. To I add dilute hydrochloric acid (5 drops) or pass in carbon dioxide; phenol separates as an oil.

(b) Take amyl alcohol (3 drops) in each of two test-tubes. To the tubes add respectively sodium hydroxide solution and water (20 drops). The alcohol is *not* more soluble in sodium hydroxide solution than in water.

5. Colours with Ferric Chloride.

Most phenols give with ferric chloride in aqueous or alcoholic solution characteristic colours (blue, green or purple) due to the formation of co-ordination compounds. Alcohols give *no* colours.

Note that compounds containing some combinations of other radicals (*e.g.*, β-keto-esters) also give coloured co-ordination compounds with ferric chloride.

(a) Dissolve phenol ($\frac{1}{2}$ spatula-point) in water (2 ml.) and add ferric chloride solution (1 drop). A violet colour is produced.

(b) Repeat (a), using ethyl alcohol (2 drops) instead of phenol. No colour is produced.

6. Millon's Reagent.

Phenols give with Millon's reagent (an aqueous solution of mercurous nitrate, mercuric nitrate and nitric acid) a red colour. Alcohols give *no* colour. The nature of the red product is unknown.

(a) Dissolve phenol ($\frac{1}{10}$ spatula-point) in water (2 ml.). Add Millon's reagent (2 ml.) and heat in a boiling water bath for 30 seconds. A red colour is produced. (Concentrated solutions of phenols give a colour in the cold.)

(b) Repeat (a), using ethyl alcohol (2 drops) instead of phenol. No colour is produced.

7. Coupling with Diazonium Salts.

Phenols couple with diazonium salts (ArN_2Cl) giving orange or red azo dyes (ArN_2Ar'). Alcohols do *not* react with diazonium salts. The diazonium salts are prepared from aromatic primary amines and nitrous acid. For details, see p. 348.

8. Oxidation by Chromic Acid.

Primary and secondary alcohols are readily oxidised by aqueous potassium dichromate and sulphuric acid to the corresponding carbonyl

layer and discard it. Wash the ethyl acetate in the separating funnel by shaking it with water (three separate 5 ml. portions), discarding the aqueous layers as before. Run the ethyl acetate into a clean, dry boiling-tube, add anhydrous calcium chloride (sufficient to fill the hemispherical part of the tube), cork and label the tube, and allow it to stand overnight. Pour the dried product through a simple filter into a dry distilling-flask and distil it. The fraction which boils between 73° and 78° is ethyl acetate.

2. Reaction with Metals.

All hydroxy compounds react with the alkali metals, giving compounds of the type RONa (alkoxides or phenoxides), hydrogen being evolved.

$$2ROH + 2Na = 2RO^-Na^+ + H_2\uparrow.$$

The alkoxides are decomposed by water, giving the alcohol and sodium hydroxide.

$$RO^-Na^+ + HOH = ROH + Na^+ + OH^-.$$

The phenoxides dissolve in water unchanged (compare reaction 4).

(a) To ethyl alcohol (2 ml.) in a porcelain basin add sodium wire (1 inch). Effervescence occurs. When it has ceased, evaporate the solution to dryness on the boiling water bath ; a white solid (sodium ethoxide) is formed.

(b) Repeat (a), using a solution of phenol (4 spatula-points) in dry ether[1] (2 ml.) instead of ethyl alcohol. Sodium phenoxide (sodium phenate) is produced. (Ether itself does *not* react with sodium, see p. 328.)

3. Reaction with Phosphorus Pentachloride.

All hydroxy compounds react with phosphorus pentachloride to give the corresponding chloro compounds, phosphorus oxychloride and hydrogen chloride. (Phenols react less readily than alcohols.) This reaction serves to distinguish alcohols and acids from ethers and esters.
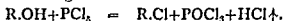
$$R.OH + PCl_5 = R.Cl + POCl_3 + HCl\uparrow.$$

(*Fume Cupboard.*) To phosphorus pentachloride (½ spatula-point) add ethyl alcohol (5 drops). A vigorous reaction occurs, fumes of hydrogen chloride being evolved.

REACTIONS WHICH DISTINGUISH BETWEEN ALCOHOLS AND PHENOLS

4. Acidic Properties of Phenols.

For explanation of reactions see the introduction to this section.

(a) Take phenol (2 spatula-points) in each of three test-tubes (I, II and III). To the tubes add the following reagents: I, sodium

---

[1] Very inflammable. Keep away from naked flames.

... : shake
... conical
... tit in a
water bath, raising the temperature gradually and collecting the dis-
tillate, which is an aqueous solution of acetaldehyde, in a receiver
surrounded by ice-water. Collect 20 ml. of distillate (*not more*),
and identify acetaldehyde in this by the preparation of its 2:4-
dinitrophenylhydrazone (see p. 331). Recrystallise your sample
of the derivative, and determine the melting-point of a mixture
of your recrystallised sample with an authentic sample of the
derivative (m.p. of acetaldehyde-2:4-dinitrophenylhydrazone is
168°).

<p align="center">SPECIAL REACTION</p>

9. The Iodoform Reaction.

Alcohols of the type $CH_3.CHOH.R$ are oxidised by hypoiodite
(iodine in alkaline solution) to the corresponding carbonyl compounds
$CH_3.CO.R$ which then undergo the iodoform reaction (see p. 335).

12, 8   THE ETHER RADICAL

Radical: $-O-$. *Class of compounds:* Ethers, R.O.R'.

Ethers are compounds in which two alkyl or aryl radicals are joined
by an oxygen atom. The ... inert.
They do *not* react with ... (con-
trast hydroxy compound ... cids,
permanganate or bromir ... and
hydriodic acids split the ether linkage to give two molecules of
hydrogen halide,

$$R.O.R' + 2HI = RI + R'I + H_2O.$$

(This reaction cannot be carried out in an elementary course.)

The ether radical is slightly water-attractive. The lower ethers are
therefore partially miscible with water, the higher ones almost im-
miscible. (Compare the solubilities in water of diethyl ether and of
n-pentane.)

<p align="center">REPRESENTATIVE COMPOUNDS</p>

Compound	m.p.	b.p.	d (g. per ml.)	s in water (g. per 100 ml.)
Diethyl ether $(C_2H_5)_2O$	−116°	35°	0·71	7
Methylphenyl ether (anisole) $CH_3.O.C_6H_5$	−37°	155°	0·99	n

compounds; the dichromate (red $Cr_2O_7^{--}$ ions) is reduced to chromic salt (green Cr^{+++} ions).

$$
\begin{array}{c}
\text{H} \\
| \\
\text{R}-\text{C}-\text{H} \\
| \\
\text{OH}
\end{array}
\quad + \quad (\text{O}) \quad = \quad
\begin{array}{c}
\text{H} \\
| \\
\text{R}-\text{C} \\
\parallel \\
\text{O}
\end{array}
\quad + \text{H}_2\text{O}.
$$

$$
\begin{array}{c}
\text{R}' \\
| \\
\text{R}-\text{C}-\text{H} \\
| \\
\text{OH}
\end{array}
\quad + \quad (\text{O}) \quad = \quad
\begin{array}{c}
\text{R}' \\
| \\
\text{R}-\text{C} \\
\parallel \\
\text{O}
\end{array}
\quad + \text{H}_2\text{O}.
$$
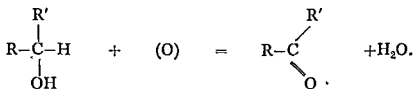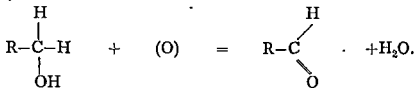
Tertiary alcohols are *not* oxidised in these conditions. Phenols undergo a complex oxidation.

(a) *Oxidation of Ethyl Alcohol.*

To ethyl alcohol (5 drops) add potassium dichromate solution (2 ml.) and concentrated sulphuric acid (5 drops). Warm the mixture gently with constant shaking. The alcohol is oxidised to acetaldehyde (smell); the solution changes colour from red to green.

(b) *Comparison of different types of Hydroxy compound.*

Repeat (a), using secondary propyl alcohol, tertiary butyl alcohol, phenol and benzyl alcohol in turn instead of ethyl alcohol.

Secondary propyl alcohol and benzyl alcohol are oxidised to carbonyl compounds. Tertiary butyl alcohol is not oxidised (the solution remains red). Phenol gives a brown complex oxidation product.

(c) *Preparation of Acetaldehyde (LARGE SCALE).*

The reaction is the same as in experiment (a). Great care must be taken in cooling the reagents during mixing, since acetaldehyde is very volatile (b.p. 21°) and is lost if the reaction mixture becomes hot before the distillation is started.

The isolation of pure acetaldehyde from the aqueous solution obtained in this preparation is too difficult to be included in an elementary course.

The preparation of the dinitrophenylhydrazone of acetaldehyde and the comparison of this with an authentic sample by the mixed melting-point method illustrate an important general method of establishing the identity of an organic compound.

To ethyl alcohol (30 ml.) in a 200-300 ml. flat-bottomed flask, cooled in ice, add slowly and with constant shaking concentrated sulphuric acid (20 ml.). When the mixture is cold, run in 1-2 ml. at a time into an aqueous solution of sodium dichromate (25%,

Reactions common to all carbonyl compounds are dealt with first, followed by those which distinguish between aldehydes and ketones. Some of the latter reactions depend on the fact that aldehydes are readily oxidised, while ketones are not.

Miscellaneous reactions of more restricted scope are treated last. Note that aromatic aldehydes (Ar.CHO) show certain differences from aliphatic aldehydes (Alk.CHO).

The carbonyl radical is water-attractive. As in the alcohol series the lowest aldehydes and ketones are miscible in all proportions with water; among the middle and higher members the solubility decreases as the size of the hydrocarbon radical increases.

The carbonyl radical has neither acidic nor basic character. Aldehydes and ketones are therefore water-neutral substances.

Formaldehyde, like several other first members of homologous series, differs considerably in its chemical properties from all other members of the series (for special reactions see pp. 416-417).

REPRESENTATIVE COMPOUNDS

Compound	m.p.	b.p.	d (g. per ml.)	s in water (g. per 100 ml.)
Aldehydes				
Formaldehyde* $H_2.CO$	−92°	−21°		v
Acetaldehyde $CH_3.CHO$	−123°	21°†	0·78	∞
Benzaldehyde $C_6H_5.CHO$ . .	−26°	180°	1·05	0·3
Ketones				
Acetone (dimethyl-ketone) $(CH_3)_2.CO$	−95°	57°	0·79	∞
Cyclohexanone $CH_2:(CH_2)_4.CO$.	−45°	157°	0·95	2
Acetophenone (methyl-phenyl ketone) $C_6H_5.CO.CH_3$ . .	20°	202°	1·03	n

* This is often met as the solid polymer (paraformaldehyde).

† Ordinary laboratory temperature is 15-20°. Acetaldehyde must therefore be kept in ice-water so as to minimise evaporation.

Y

REACTIONS

1. Inertness towards Sodium.

Ethers do *not* react with sodium. Contrast hydroxy compounds (p. 324).

> To diethyl ether[1] (1 ml.) add sodium wire (1 inch). No reaction occurs. Now add ethyl alcohol (1 ml.) to react with the sodium, before throwing the mixture into the sink.

2. Inertness towards Phosphorus Pentachloride.

Ethers do *not* react with phosphorus pentachloride in the cold. Contrast hydroxy compounds (p. 324).

> (*Fume Cupboard.*) To phosphorus pentachloride ($\frac{1}{4}$ spatula-point) add diethyl ether[1] (1 ml.). No reaction occurs.

3. Inertness towards Alkalis.

Ethers are *not* hydrolysed by alkalis. Contrast esters (p. 342).

> Reflux anisole (2 ml.) with bench sodium hydroxide solution (25 ml.) for half an hour. The anisole remains unchanged (note quantity and smell).

4. Colour of Iodine Solutions.

Ethers can be distinguished from hydrocarbons by the colours of their iodine solutions. Solutions of iodine in compounds containing only carbon and hydrogen or carbon, hydrogen and halogen are *red* or *violet*. Solutions of iodine in organic compounds containing oxygen or nitrogen in any form are *brown*.

> In four *dry* ignition-tubes take respectively pentane, pentene, benzene, diethyl ether (1 ml. each). To each tube add iodine ($\frac{1}{16}$ spatula-point) and shake. The colours obtained are as follows : pentane, violet ; pentene, pink (fades) ; benzene, red violet (fades on long standing) ; diethyl ether, brown.

12, 9   THE CARBONYL RADICAL

Radical: $\diagup$ C=O.

Classes of compounds:

Aldehydes, $\begin{array}{c} R \\ \diagup \\ C=O \\ \diagup \\ H \end{array}$ or R.CHO ;   Ketones, $\begin{array}{c} R \\ \diagup \\ C=O \\ \diagup \\ R' \end{array}$ or R.CO.R'.

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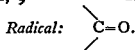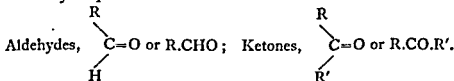
[1] Very inflammable. Keep away from naked flames.

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REPRESENTATIVE COMPOUNDS

Compound	m.p.	b.p.	d (g.perml.)	s in water (g. per 100 ml.)
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Cyclohexanone $CH_2.(CH_2)_4.CO$	−45°	157°	0·95	2
Acetophenone (methyl-phenyl ketone) $C_6H_5.CO.CH_3$	20°	202°	1·03	n

* This is often met as the solid polymer (paraformaldehyde).

† Ordinary laboratory temperature is 15-20°. Acetaldehyde must therefore be kept in ice-water so as to minimise evaporation.

REACTIONS

REACTIONS COMMON TO ALL CARBONYL COMPOUNDS

**1. Condensation with Various Compounds containing —NH₂
Radicals.**

Carbonyl compounds condense with many compounds containing
the radical —NH₂ with elimination of water, as follows:

$$\begin{array}{c} R \\ \diagdown \\ C=O \\ \diagup \\ R' \end{array} \quad +H_2N.Q \quad = \quad \begin{array}{c} R \\ \diagdown \\ C=N-Q \\ \diagup \\ R' \end{array} \quad +H_2O.$$
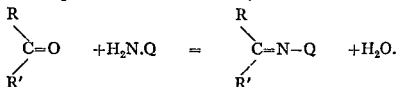
R and R' may be alkyl, aryl, or hydrogen.

Some common reagents H₂N.Q and their condensation-products are
tabulated below. Many of the products are useful for the identification
of carbonyl compounds. The reactions are dealt with in detail here,
not on account of their intrinsic importance, but because they are
among the most convenient examples of derivative-formation for an
elementary course.

Reagents H₂N.Q which Condense with Carbonyl Compounds

Reagent H₂N.Q	Condensation Product RR'C:N.Q	Value of Condensation Product for Identification of Carbonyl Compounds
Primary alkyl or aryl amine, H₂N.R″	Schiff's bases	Little (but see pp. 347, 401, and 433 for other uses of this reaction)
Hydroxylamine H₂NOH	Oximes	Considerable (for carbonyl compounds of higher M.W.)
Hydrazine H₂N.NH₂	Hydrazones	Very little (many derivatives are liquids)
Phenylhydrazine H₂N.NH.C₆H₅	Phenylhydrazones	Great (especially for carbohydrates, see pp. 384-386)
2:4-Dinitrophenyl-hydrazine H₂N.NH.C₆H₃.(NO₂)₂	2:4-Dinitrophenyl-hydrazones	Great
Semicarbazide H₂N.NH.CONH₂	Semicarbazones	Great

Derivatives of Representative Compounds

Carbonyl Compound	Derivatives (m.p., if solid : colour, if any)			
	Oxime	*Phenyl-hydrazone*	*2:4-Dinitro-phenyl-hydrazone*	*Semi-carbazone*
Formaldehyde .	liquid	liquid	168° yellow	169° (dec)
Acetaldehyde .	47°	63°	168° yellow	163°
Benzaldehyde .	35°	158°	237° orange	227° (dec)
Acetone . .	60°	42°	126° orange	188°
Cyclohexanone .	91°	77°	162° yellow	166°
Acetophenone .	59°	105°	249° orange-red	198°

dec=decomposes.

Note that reagents of higher molecular weight give derivatives of higher melting-point and are therefore more generally useful. (Compare semicarbazones and oximes, or 2:4-dinitrophenylhydrazones and phenylhydrazones.)

(a) Preparation of 2:4-Dinitrophenylhydrazones in Aqueous Solution.

Carbonyl compounds which are soluble in water are treated with a saturated solution of 2:4-dinitrophenylhydrazine in 2M aqueous hydrochloric acid, called here "Aqueous DNPH Reagent."

To Aqueous DNPH Reagent (20 ml.) add the carbonyl compound (*e.g.*, acetaldehyde or acetone) (5 drops) and shake. A copious yellow precipitate is immediately formed. Filter this by suction, and wash with water until the washings are free from acid. Dry the precipitate as thoroughly as possible by suction on the filter, recrystallise it from ethyl alcohol and determine the melting-point of the product.

(b) Preparation of 2:4-Dinitrophenylhydrazones in Alcoholic Solution.

Carbonyl compounds which are insoluble in water but soluble in ethyl alcohol are treated with a saturated solution of 2:4-dinitrophenyl-hydrazine in ethyl alcohol, called here "Alcoholic DNPH Reagent," and a trace of mineral acid. The Alcoholic Reagent is used, since with the Aqueous Reagent there would be little contact between the carbonyl

compound and the hydrazine, and hence reaction, if it took place at all, would be slow.

The carbonyl compound (if liquid, *e.g.*, benzaldehyde, 5 drops; if solid, *e.g.*, acetophenone, 5 spatula-points), ethyl alcohol (5 ml.) and Alcoholic DNPH Reagent (5 ml.) are mixed and boiled in the water bath. Concentrated hydrochloric acid (3 drops) is then added, and the mixture is boiled for half a minute in the water bath and cooled. The precipitate which forms is filtered by suction, washed with a little cold ethyl alcohol and recrystallised. (Ethyl acetate is often useful for the recrystallisation of these derivatives.)

(c) *Preparation of a Phenylhydrazone.*

Mix phenylhydrazine (10 drops), glacial acetic acid (10 drops), water (5 ml.), and benzaldehyde (10 drops), and shake. Benz-aldehyde-phenylhydrazone separates as a white solid which may be recrystallised from ethyl alcohol.

(d) *Preparation of a Semicarbazone.*

Dissolve semicarbazide hydrochloride (10 spatula-points) in saturated aqueous sodium acetate solution (2 ml.). Add acetone (10 drops) and shake. Acetone-semicarbazone separates as a white solid, which may be recrystallised from ethyl alcohol.

2. Addition Reactions.

Many reagents add across the double bond of the carbonyl radical thus :

$$
\begin{array}{c} R \\ \diagdown \\ C=O \\ \diagup \\ R' \end{array}
\; + HZ \; = \;
\begin{array}{c} R \quad OH \\ \diagdown \diagup \\ C \\ \diagup \diagdown \\ R' \quad Z \end{array}
$$
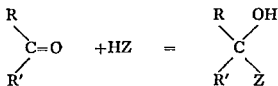
(R and R' may be alkyl, aryl, or hydrogen.)

The only reagent of this type which can be used here is sodium bisulphite ($NaHSO_3$), which gives addition compounds of the general formula :

$$
\begin{array}{c} R \quad OH \\ \diagdown \diagup \\ C \\ \diagup \diagdown \\ R' \quad SO_3Na \end{array}
$$
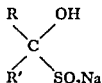
These are solids which can be used for the separation and purification of many carbonyl compounds. They cannot be used for identifica-

tion since they do not melt. (Some ketones do not form bisulphite compounds.)

To saturated aqueous sodium bisulphite solution (2 ml.) add acetone (10 drops) and shake. A white precipitate forms, and the mixture becomes warm. On cooling the mixture under the tap, the precipitate increases in quantity.

REACTIONS WHICH DISTINGUISH BETWEEN ALDEHYDES AND KETONES

3. Oxidation.

Aldehydes are oxidised by mild oxidising agents to carboxylic acids with the *same* number of carbon atoms.

$$R-\overset{\displaystyle H}{\underset{\displaystyle O}{C}} \quad +(O) \quad = \quad R-\overset{\displaystyle OH}{\underset{\displaystyle O}{C}}$$
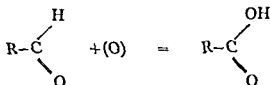
Ketones are *not* oxidised in these conditions.

The mild oxidising agents generally used are alkaline solutions of silver and cupric salts, which are reduced to metallic silver and cuprous oxide respectively. The alkaline silver salt solution is ammoniacal silver nitrate, which contains the hydroxide of the complex silver-ammonia ion, $[Ag.2NH_3]OH$. The alkaline copper salt solution is Fehling's reagent, which contains a complex copper tartrate. The reductions may conveniently be represented as follows :

$$Ag_2O \quad = \quad 2Ag+(O).$$
$$2CuO \quad = \quad Cu_2O+(O).$$
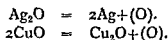
Fehling's reagent is unstable and must therefore be prepared fresh each day by mixing equal volumes of the two components, viz. Fehling's Solution No. 1 (containing copper sulphate) and Fehling's Solution No. 2 (containing ...

Ammoniacal Silver Nitrate.

(a) To silver nitrate solution (0·1M, 2 ml.) add dilute ammonia *dropwise* until the precipitate of silver oxide which first forms *just* disappears. Add acetaldehyde (2 drops) and heat the mixture in the boiling water bath for half a minute. A mirror of metallic silver is formed on the walls of the tube.

(b) Repeat, using acetone (2 drops) instead of acetaldehyde. No reduction occurs.

Fehling's Solution.

(*c*) Mix Fehling's Solution No. 1 (1 ml.) and Fehling's Solution No. 2 (1 ml.) ; to the deep blue solution so obtained add acetaldehyde (2 drops) and boil. A red or yellow precipitate of cuprous oxide is formed.

(*d*) Repeat, using acetone (2 drops) instead of acetaldehyde. No reduction occurs.

4. Schiff's Reagent.

Schiff's reagent is a solution of magenta which has been decolorised by sulphur dioxide. Aldehydes colour the reagent pink, ketones do *not*. (The mechanism of the reaction is complicated.)

To Schiff's reagent (separate 2 ml. portions) add the following carbonyl compounds—acetaldehyde, benzaldehyde, acetone (2 drops each). Pink colours are produced with the first two compounds but not with acetone.

<div align="center">MISCELLANEOUS REACTIONS</div>

5. Reaction with Nitroprusside.

Many carbonyl compounds containing the grouping .CH$_2$.CO. give intense colours with sodium nitroprusside, Na$_2$[Fe(CN)$_5$(NO)] in aqueous solution. (The chemistry of the reaction is unknown.)

In purely chemical work the reaction is carried out as described below; the solution being first made alkaline with sodium hydroxide and then acidified with glacial acetic acid.

Colours obtained are approximately as follows :

	Solution alkaline (NaOH)	Solution acidic (acetic acid)
Aliphatic aldehydes Alk.CHO . .	red	colour fades
Aromatic aldehydes Ar.CHO. .	none	none
Aliphatic ketones Alk.CO.Alk' .	red	red-violet
Mixed aliphatic-aromatic ketones	red or	violet or
Alk.CO.Ar	violet-red	blue
Aromatic ketones Ar.CO.Ar' . .	none	none

A modification of the test, in which the solution is saturated with ammonium sulphate and made alkaline with ammonia is used clinically to detect acetone and related substances in urine (for details see p. 424).

Carry out the following test with acetaldehyde, acetone, and acetophenone:

To the carbonyl compound (1 drop) add water (2 ml.), sodium nitroprusside (5% aqueous solution, 10 drops), sodium hydroxide (2M, 3 drops). Shake and stand for one minute. Note the colour produced ; then add glacial acetic acid (10 drops) and note the change in colour.

6. The Iodoform Reaction.

Compounds of the type $CH_3.CO.R$, where R may be alkyl, aryl, or hydrogen, yield iodoform (CHI_3) on treatment with iodine in aqueous alkali. The reaction may be represented as follows :—

$$CH_3.CO.R + 3I_2 \rightleftharpoons CI_3.CO.R + 3HI \text{ (halogenation).}$$
$$CI_3.CO.R + NaOH \rightleftharpoons CHI_3 + R.COONa \text{ (hydrolysis).}$$
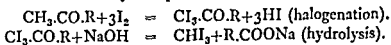
(a) To acetone (2 drops) add iodine (solution in aqueous potassium iodide, 5 ml.) followed by sodium hydroxide solution . . . . (smell).

Compounds of the type $CH_3.CHOH.R$ also give iodoform in this test on heating, since they are first oxidised to the corresponding carbonyl compounds, and then halogenated and hydrolysed as above.

(b) Repeat experiment (a), using ethyl alcohol (5 drops) instead of acetone (2 drops). When the colour of the iodine is almost discharged, heat in the boiling water bath for one minute and cool. Iodoform is produced only on heating.

A corresponding reaction using chlorine in place of iodine serves for the preparation of chloroform. The reagent used is an aqueous suspension of bleaching powder, $Ca(OCl)Cl + Ca(OH)_2$.

(c) Take bleaching powder (sufficient to cover the bottom of a boiling-tube), add water (5 ml.) and mix with a glass rod to form a smooth paste. Add acetone (2 drops), shake, and warm *very gently*. The mixture froths and smells of chloroform.

7. Reaction with Sodium Hydroxide.

Aliphatic aldehydes on boiling with sodium hydroxide give a yellow or brown evil-smelling resinous condensation product. Aldehydes in which the CHO radical is directly attached to an aromatic nucleus undergo the following change (Cannizzaro reaction) on treatment with strong alkali.

$$2 Ar.CHO + OH^- \rightleftharpoons Ar.CH_2OH + Ar.COO^-.$$
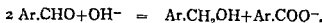
Such reactions, in which one molecule of the starting material is oxidised, while another is reduced, are called *dismutations*.
Ketones are *not* affected by boiling with strong alkali. (For special behaviour of formaldehyde see p. 417.)

(a) Boil together acetaldehyde (5 drops) and sodium hydroxide solution (2 ml.). A yellow or brown evil-smelling resin is formed.

(b) Repeat (a), using acetone (5 drops) instead of acetaldehyde. No change occurs.

8. Reversible Polymerisation by Acid.

Many aliphatic aldehydes on treatment with a trace of concentrated sulphuric acid in the cold polymerise. The product formed from acetaldehyde is a cyclic acetal (paraldehyde) which is sparingly soluble in water. On heating with dilute acid the polymeride is decomposed and acetaldehyde re-formed. Ketones do *not* polymerise in these conditions.
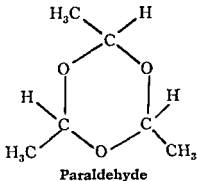
Paraldehyde

(a) To acetaldehyde (1 ml.) add concentrated sulphuric acid (1 drop) and shake. Note the evolution of heat and change of smell. Add water (3 ml.); the reaction product is immiscible with this. Warm the mixture; it becomes homogeneous and once more smells of acetaldehyde.

(b) Repeat (a), using acetone (1 ml.) instead of acetaldehyde. No changes take place.

12, 10   THE CARBOXYL RADICAL

Radical:

O—H or —COOH.
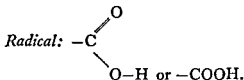
Class of compounds: Carboxylic Acids,

O—H or R.COOH, and their salts.
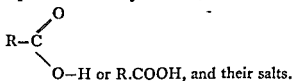
The carboxyl radical is the most important *acidic* radical found in organic compounds. All the simple monocarboxylic acids are weak acids, the hydrogen of the carboxyl radical ionising in aqueous solution to a slight extent thus :

$$R.COOH \rightleftharpoons R.COO^- + H^+.$$
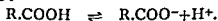
pK_a values for representative acids are given in the table below. The acids in aqueous or alcoholic solution redden blue litmus.

The carboxyl radical is water-attractive. The lower acids are therefore miscible with water in all proportions; the solubility of the medium and higher acids decreases as the size of the hydrocarbon radical increases.

The radical R.CO is called an *acyl* radical.

The acids react with bases to give salts, many of which, including the alkali and ammonium salts, are strong electrolytes:

$$R.COOH + OH^- \rightleftharpoons R.COO^- + HOH.$$
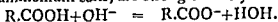
Many salts are readily soluble in water and insoluble in non-ionising solvents (*e.g.*, ether), even though their parent acids are ether soluble and water insoluble. Many acids which are insoluble in water can therefore be "dissolved" in sodium hydroxide solution.

Since the acids are stronger than carbonic acid (pK_a (first stage)= 6·37; pK_a (second stage)=10·25) they displace it from its salts and dissolve as readily in sodium carbonate or bicarbonate solution as in sodium hydroxide solution (contrast phenols, pp. 321, 324-325).

$$R.COOH + HCO_3^- \rightleftharpoons R.COO^- + CO_2 + H_2O.$$
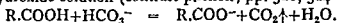
The metallic salts of the carboxylic acids are all non-volatile solids. The ammonium salts are solids, which on heating dissociate into ammonia and the free acid, $R.COO-NH_4^+ \rightleftharpoons R.COOH + NH_3$. The alkali metal salts of the aliphatic acids containing 12 or more carbon atoms when dissolved in water are colloidal electrolytes and have detergent properties. Ordinary soap is a mixture of such salts (*e.g.*, sodium stearate $C_{17}H_{35}.COO-Na^+$).

Strong acids displace the carboxylic acids from their salts in aqueous solution, $R.COO^- + H^+ \rightleftharpoons R.COOH$. The carboxylic acids are precipitated (if insoluble in water) or may be distilled off (if volatile).

Since the acids are weak, their salts with strong bases are hydrolysed in solution and react alkaline to litmus (see p. 95).

$$R.COO^- + Na^+ + H^+ + OH^- \rightleftharpoons R.COOH + Na^+ + OH^-.$$
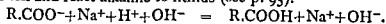
Formic acid, as well as showing the general reactions of the carboxyl radical, has certain specific reactions (see pp. 418-419).

REPRESENTATIVE COMPOUNDS

Compound	m.p.	b.p.	d (g. per ml.)	s in water (g. per 100 ml.)	pK_a
Formic acid H.COOH	8°	101°	1·22	∞	3·75
Acetic acid CH₃.COOH	17°	118°	1·05	∞	4·75
Heptoic acid CH₃.(CH₂)₅.COOH	−10°	224°	0·91	0·2	4·85
Stearic acid CH₃.(CH₂)₁₆.COOH	69°	232° (15 mm)	0·94	0·03	
Benzoic acid C₆H₅.COOH . .	122°	249°	1·27	0·3	4·20

The sodium, potassium and ammonium salts of these acids are all odourless solids ; they are readily soluble in water with the exception of the stearates, which are much less soluble.

<div style="text-align:center">REACTIONS</div>

<div style="text-align:center">IONIC REACTIONS</div>

1. Acidic Properties.

For discussion of reactions see the introduction to this section.

(a) Formation of Salts from Carboxylic Acids and Bases.

Carry out the following experiment with acetic acid, heptoic acid and benzoic acid in turn. The approximate quantities of the acids required are as follows :—glacial acetic acid (12 drops), heptoic acid (30 drops), benzoic acid (1·2 g.). Note that heptoic acid and benzoic acids, which the preliminary examination has shown to be sparingly soluble in water, are readily " soluble " in sodium hydroxide, due to the formation of their sodium salts.

> Take in a porcelain basin dilute sodium hydroxide (approximately 2M, 5 ml.) and phenolphthalein (2 drops). Add the acid (liquid from dropping-pipette, solid from spatula) with stirring until the indicator is just decolorised. Evaporate the solution to dryness on the boiling water bath. The sodium salt of the acid remains as an odourless white solid. Keep this for subsequent reactions.

(b) Formation of Salts from Carboxylic Acids by displacement of a Weaker Acid (Carbonic Acid).

Carry out the following experiment with acetic acid, heptoic acid and benzoic acid in turn.

> To sodium bicarbonate solution (2 ml.) add the acid (liquids, 5 drops ; solid, 5 spatula-points). The acid " dissolves " due to the formation of its sodium salt, and carbon dioxide is evolved.

(c) Displacement of Carboxylic Acids from their Salts by Strong Acids.

Carry out the following experiment with sodium acetate, sodium heptoate and sodium benzoate (prepared in (a)) in turn.

> Dissolve the salt (2 spatula-points) in water (2 ml.) and add dilute sulphuric acid (2 ml.). The carboxylic acids are liberated ; heptoic and benzoic acids, being sparingly soluble in water, separate from solution ; acetic acid, being miscible with water in all proportions, does not separate but its smell is perceptible.

(d) pH Values of Acid Solutions.

For comparison of *p*H values of a carboxylic acid and a strong mineral acid at different dilutions, see pp. 164-165.

(e) Determination of the Equivalent of an Acid.

See pp. 144-145.

2. Precipitation Reactions of Carboxylate Anions.

The precipitation reactions of the carboxylate anions in aqueous solution are of less interest than those of the inorganic anions. The reactions [1] with ferric ions help to distinguish between different types of carboxylic acid anions, but not between individual anions (see (a) below, and under hydroxy acids, pp. 422 and 431). Anions of lower aliphatic monocarboxylic acids give deep red colours due to the formation of soluble complex ferric salts. Anions of aromatic acids give buff precipitates of insoluble ferric salts.

The alkali metal salts of the higher fatty acids (soaps) are salted out of their aqueous solutions by soluble inorganic salts containing the same cation (common ion effect, see pp. 86–87). The other salts of these acids are almost insoluble in water, and are therefore precipitated in double decomposition reactions (e.g., precipitation of calcium and magnesium stearates, reaction (c); this occurs when soap is put into hard water).

(a) Reactions with Ferric Chloride Solution.

Take in three test-tubes sodium acetate (2 spatula-points from experiment 1 (a), in 2 ml. water), sodium benzoate (2 spatula-points, in 2 ml. water), water (2 ml.), for blank test. To each tube add ferric chloride solution (3 drops). A deep red colour is produced in the acetate solution (contrast blank test), and a buff precipitate in the benzoate solution.

(b) Salting-out of Sodium Stearate.

To sodium stearate solution (2 ml.), add saturated sodium chloride solution (2 ml.). A white curd of sodium stearate separates.

(c) Precipitation of Calcium and Magnesium Soaps.

To sodium stearate solution (2 ml. in each of two test-tubes) add respectively calcium chloride and magnesium sulphate solutions (2 ml. each). White curds of calcium and magnesium stearates separate.

3. Reactions of Cations of Salts.

The cations of the salts of carboxylic acids in aqueous solution give their usual reactions. A reaction of particular importance is that of ammonium salts with sodium hydroxide, ammonia being liberated in the cold (contrast amides, see pp. 350–351).

Show that solutions of calcium acetate and lead acetate give the usual reactions of their cations.

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[1] These reactions must be carried out in neutral solution. If a solution of a free acid has to be tested, it may be neutralised by adding an excess of dilute ammonia and boiling until the mixture no longer smells of ammonia.

OTHER REACTIONS

4. Esterification.

This has been considered among the reactions of the hydroxyl radical (pp. 322-324).

Salts of carboxylic acids on heating with concentrated sulphuric acid and an alcohol yield esters. The sulphuric acid first liberates the carboxylic acid, and then catalyses its esterification.

> To sodium acetate (1 spatula-point) add ethyl alcohol (2 ml.) and concentrated sulphuric acid (10 drops). Continue as in experiment 1 (a), p. 323; ethyl acetate is produced (smell).

5. Reaction with Phosphorus Pentachloride.

Carboxylic acids react with phosphorus pentachloride to give acid chlorides, phosphorus oxychloride and hydrogen chloride (compare alcohols, contrast ethers and esters).

$$R-C{\overset{\displaystyle O}{\underset{\displaystyle OH}{}}}\ +PCl_5\ =\ R-C{\overset{\displaystyle O}{\underset{\displaystyle Cl}{}}}\ +POCl_3+HCl\uparrow.$$
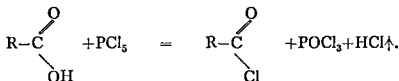
> (*Fume Cupboard.*) (a) To phosphorus pentachloride ($\frac{1}{4}$ spatula-point) add glacial acetic acid (3 drops). A vigorous reaction occurs with evolution of hydrogen chloride.
>
> (b) Repeat, using heptoic acid instead of acetic acid. A similar reaction occurs.

6. Decarboxylation.

Carboxylic acids and their salts when heated with soda lime[1] yield hydrocarbons.

$$R.COONa+NaOH\ =\ R.H+Na_2CO_3.$$

> Mix intimately in an ignition-tube benzoic acid (2 spatula-points) and soda-lime (10 spatula-points) and heat. A colourless liquid (benzene) condenses in the cooler part of the tube.

12, 11   THE ESTER RADICAL

$$Radical:\ -C{\overset{\displaystyle O}{\underset{\displaystyle O-}{}}}$$

$$Class\ of\ compounds:\ Esters,\ R-C{\overset{\displaystyle O}{\underset{\displaystyle O-R'}{}}}\ \ or\ R.COOR'.$$

---
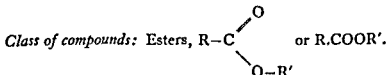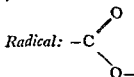
[1] Made by slaking quicklime with aqueous sodium hydroxide.

Esters are compounds obtained by the interaction of a hydroxy compound and a carboxylic acid [1] with elimination of water thus:

$$R-C{\overset{O}{\underset{O-H}{}}} \quad +HOR' \quad = \quad R-C{\overset{O}{\underset{O-R'}{}}} \quad +HOH$$
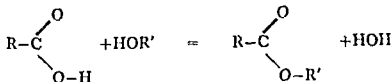
e.g., acetic acid+ethyl alcohol=ethyl acetate+water.

Although the names of the esters seem to imply that these substances are analogous to salts (compare the names " ethyl acetate," " sodium acetate "), the esters are compounds of a completely different type. They do *not* ionise, and (with a few exceptions of low molecular weight) they are sparingly soluble in water, since the ester radical is but slightly water-attractive. The esters are *neutral* substances.

The most important reaction of esters is their hydrolysis by alkali or acid (usually the former) to give the carboxylic acids and alcohols (or phenols) from which they are derived. This hydrolysis is usually slow at room temperature, and there is as a rule no visible change when esters are added to cold dilute alkali or acid.

REPRESENTATIVE COMPOUNDS

Compound	m.p.	b.p.	d (g. per ml.)	s in water (g. per 100 ml.)
Ethyl acetate $CH_3.COOC_2H_5$.	−84°	77°	0·90	9
Ethyl benzoate $C_6H_5.COOC_2H_5$.	−35°	213°	1·05	0·08
Phenyl acetate $CH_3.COOC_6H_5$.		196°	1·08	v.sl
Phenyl benzoate $C_6H_5.COOC_6H_5$.	70°	314°	1·24	v.sl

REACTIONS

1. Covalent Linkage between Acyl and Alkyl or Aryl Radicals.

The linkage between the acyl and alkyl or aryl groups in an ester is covalent ; accordingly the ester in the presence of water does *not* give rise to th~~e anions of th~~

is .... drops) ; a clear solution
.... solution (2 drops). No
red colour due to the presence of acetate ions is produced. Carry out *positive* and *negative control* tests for acetate ions, using an aqueous solution of sodium acetate and water respectively.

[1] Esters of inorganic acids may also be obtained (see p. 429).

2. Hydrolysis by Alkali.

Esters are hydrolysed by aqueous or alcoholic sodium hydroxide to give (i) the sodium salt of a carboxylic acid, and (ii) an alcohol (or, if the ester is derived from a phenol, the sodium derivative of the latter). Treatment of the product with a strong mineral acid yields the carboxylic acid itself (and the phenol itself, if the ester is derived from a phenol).

Ethyl benzoate thus gives ethyl alcohol and sodium benzoate, from which benzoic acid is formed by treatment with dilute mineral acid.

Hydrolysis : $C_6H_5.COOC_2H_5 + OH^- = C_6H_5.COO^- + C_2H_5OH$.

Acidification : $C_6H_5.COO^- + H^+ = C_6H_5.COOH\downarrow$.
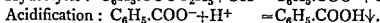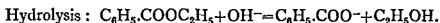
Ethyl alcohol may be distilled away from the reaction-mixture before acidification.

Phenyl acetate gives sodium phenoxide and sodium acetate, which with dilute mineral acid yield phenol and acetic acid.

Hydrolysis : $CH_3.COOC_6H_5 + 2OH^- = CH_3.COO^- + C_6H_5O^-$.

Acidification : $\begin{cases} CH_3.COO^- + H^+ = CH_3.COOH. \\ C_6H_5O^- + H^+ = C_6H_5OH. \end{cases}$
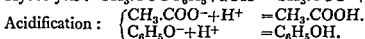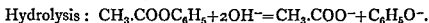
Contrast inertness of ethers (p. 328).

The hydrolysis of most esters requires thirty minutes' or more heating. The reaction cannot therefore be done in a test-tube without a reflux-condenser.

Hydrolysis of Ethyl Benzoate (LARGE SCALE).

Fit up an apparatus for reflux (Fig. 4, p. 30). Run into the conical flask ethyl benzoate (2 ml.) and sodium hydroxide solution (25 ml.). Add three porous chips and reflux the mixture gently c . . . .
e . . . .
7 . . . .

Disconnect the condenser and reattach it to the flask by means of a bent tube in the position . . . . (p. 44). Distil about 5 ml. o . . . . solution of ethyl alcohol. (Test it by oxidation with dichromate to acetaldehyde (smell) and by the iodoform reaction.)

Disconnect and cool the flask, and acidify the liquid in it with bench dilute sulphuric acid. A dense white precipitate of benzoic acid is formed. Filter this by suction, wash it with water and recrystallise about one-quarter of it from boiling water. Dry the recrystallised material by pressing it between sheets of filter-paper, and determine its melting-point.

3. Reaction with Ammonia.

Some esters on treatment with concentrated aqueous ammonia yield amides (compounds containing the radical $.CONH_2$).

$$R-\overset{\overset{O}{\|}}{C}\underset{O-R'}{}+NH_3 \ = \ R-\overset{\overset{O}{\|}}{C}\underset{NH_2}{}+R'OH.$$
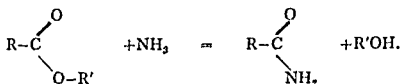
Preparation of Acetamide (LARGE SCALE).

Mix ethyl acetate (10 ml.) and concentrated aqueous ammonia ($d=0.880$; 10 ml.) in a boiling-tube, and leave the tube loosely stoppered in your cupboard. The two layers gradually form a homogeneous liquid. After the mixture has stood for a week, transfer it to a distilling-flask and distil it slowly. The liquid distilling up to 130° consists of ethyl alcohol, ammonia, and water, and is discarded. Remove the water-condenser, and continue the distillation, using the side-arm of the distilling-flask as an air-condenser, and a boiling-tube fitting over it as a receiver. When the boiling-point of the distillate reaches 210°, change receivers. The material distilling between 210° and 225° is acetamide, which solidifies on cooling.

4. Inertness towards Phosphorus Pentachloride.

Esters do *not* react with phosphorus pentachloride in the cold (contrast alcohols and acids, but compare ethers).

To phosphorus pentachloride ($\frac{1}{4}$ spatula-point) add ethyl acetate (1 ml.). No reaction occurs.

12, 12   THE AMINE RADICALS

Radicals: $-NH_2$ (amino), $\overset{}{\underset{}{}}NH$ (imino), $\overset{}{\underset{}{}}N$.

Classes of compounds: Amines (primary, secondary and tertiary; $R.NH_2$, $RR'NH$, $RR'R''N$), and their salts.

The amines are the most important class of *basic* organic compounds. Their chemistry is simple if they are considered as substituted ammonias, thus:

NH_3	RNH_2	$RR'NH$	$RR'R''N$
ammonia	primary amine	secondary amine	tertiary amine
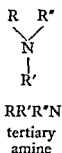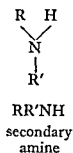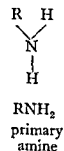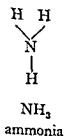
Just as ammonia dissolves in water, giving the weak base ammonium hydroxide:

$$NH_3 + H_2O \quad \rightleftharpoons \quad NH_4OH \quad \rightleftharpoons \quad NH_4^+ + OH^-,$$
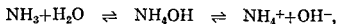
so any amine which dissolves in water gives a substituted ammonium hydroxide, which is also a weak base, e.g.,

$$RNH_2 + H_2O \quad \rightleftharpoons \quad RNH_3OH \quad \rightleftharpoons \quad RNH_3^+ + OH^-.$$
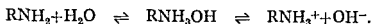
The amines in aqueous solution therefore turn red litmus blue. pK_b values for representative amines are given below; note that aromatic amines are much weaker bases than aliphatic amines.

The amine radicals are water-attractive; the lower amines are therefore extremely soluble in water, and the solubility decreases as the size of the hydrocarbon radicals in the compounds increases.

Furthermore, just as ammonia reacts with an acid (e.g., hydrochloric acid) to give a salt (e.g., ammonium chloride) thus:

$$\begin{array}{c} H \quad H \\ \diagdown \; \diagup \\ N \\ | \\ H \end{array} \;\; +H^+ + Cl^- \;\;=\;\; \begin{bmatrix} H \quad H \\ \diagdown \; \diagup \\ N \\ \diagup \; \diagdown \\ H \quad H \end{bmatrix}^+ \;\; +Cl^-$$
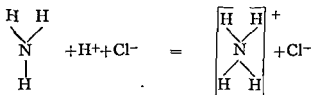
so any amine reacts with an acid (e.g., hydrochloric acid) to give a substituted ammonium salt (e.g., substituted ammonium chloride or amine hydrochloride), thus:

$$\begin{array}{c} H \quad H \\ \diagdown \; \diagup \\ N \\ | \\ R' \end{array} \;\; +H^+ + Cl^- \;\;=\;\; \begin{bmatrix} H \quad H \\ \diagdown \; \diagup \\ N \\ \diagup \; \diagdown \\ R' \quad H \end{bmatrix}^+ \;\; +Cl^-$$
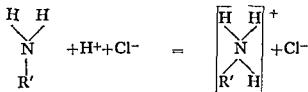
Many of these salts are strong electrolytes, which are readily soluble in water and almost insoluble in non-ionising solvents such as ether,[1] even if the parent base is sparingly soluble in water and readily soluble in ether. Many amines which are insoluble in water can therefore be " dissolved " by hydrochloric acid.

The amine hydrohalides are solids, which, on heating, decompose into the amine and the acid from which they were formed (compare ammonium salts). Strong bases displace the amines from their salts in aqueous solution.

$$RNH_3^+ + OH^- \quad = \quad RNH_2 + H_2O.$$

The amines are precipitated (if insoluble in water) or can be expelled from the solution by boiling (if volatile).

Since the amines are weak bases, their salts with strong acids (e.g.,

[1] Certain amine salts are, however, soluble in chloroform.

hydrochloric acid) are hydrolysed in solution and react acidic to litmus (see p. 96).

$$RNH_3^+ + Cl^- + H^+ + OH^- \;=\; RNH_2 + HOH + H^+ + Cl^-.$$

Note that amines in their behaviour as bases resemble carboxyl compounds in their behaviour as acids.

The above-mentioned reactions are common to *all* amines and are their most important chemical properties. There are other reactions which enable us to distinguish between primary, secondary and tertiary amines, and in the case of primary amines there are marked differences between the alkyl and aryl compounds (Alk.NH$_2$ and Ar.NH$_2$) (see reactions 5, 6 and 7).

Salts of the type $R_4N^+Hal^-$, called quaternary ammonium salts, can be prepared ; the corresponding bases $R_4N^+OH^-$ are strong.

Quaternary ammonium salts containing a long-chain alkyl radical (*e.g.*, cetyltrimethylammonium bromide, $C_{16}H_{33}N(CH_3)_3^+Br^-$) act as detergents like the salts of long-chain carboxylic acids (*e.g.*, sodium stearate, $C_{17}H_{35}.COO^-Na^+$) and are called " invert soaps."

REPRESENTATIVE COMPOUNDS

Compound	m.p.	b.p.	*d* (g. per ml.)	s in water (g. per 100 ml.)	pK_b
Methylamine $CH_3.NH_2$ . .	$-92°$	$-6°$		160	3·36
Dimethylamine $(CH_3)_2NH$.	$-96°$	$7°$		v	3·28
Trimethylamine $(CH_3)_3N$.	$-124°$	$4°$		92	3·26
Phenylamine (aniline) $C_6H_5.NH_2$.	$-6°$	$184°$	1·02	3	9·40
Methylphenylamine* (methylaniline) $C_6H_5.NH.CH_3$.	$-57°$	$196°$	0·99	v.sl	9·60
Diphenylamine $(C_6H_5)_2NH$	$53°$	$302°$	1·16	0·03	
Dimethylphenyl-amine (dimethyl-aniline)* $C_6H_5.N(CH_3)_2$	$3°$	$193°$	0·96	v.sl	9·62
Benzylamine $C_6H_5.CH_2.NH_2$		$185°$	0·98	∞	4·62

* Yellow ; all the other compounds listed are colourless.

The hydrochlorides of all these amines are white solids, soluble in water. (Many are extremely soluble.)

1. Basic Properties.

For discussion of reactions see introduction to this section.

(a) *Formation of Salts from Amines and Acids.*

Carry out the following reaction with methylamine (approximately 2M aqueous solution, 5 ml.) and aniline (20 drops) in turn. Note that aniline, which the preliminary examination has shown to be sparingly soluble in water, is readily "soluble" in hydrochloric acid due to the formation of its hydrochloride.

> Take in a porcelain basin the amine, and add from a graduated pipette dilute hydrochloric acid until the mixture is just acid to Congo red paper.[1] Evaporate the solution to dryness on the boiling water bath. The amine hydrochloride remains as an odourless residue. Show that this gives the reactions of chloride ion.

(b) *Displacement of Amines from their Salts by Strong Bases.*

Carry out the following experiment with methylamine hydrochloride and aniline hydrochloride (prepared in (a)), and with ammonium chloride for comparison:

> Dissolve the salt (2 spatula-points) in water (2 ml.) and add sodium hydroxide (2 ml.). The amine (or ammonia) is liberated; aniline, being sparingly soluble in water, separates from solution; since methylamine and ammonia are soluble in water but volatile, they do *not* separate but their smell is perceptible.

(c) *Determination of the Equivalent of an Amine.*

See pp. 148-149.

2. Precipitation Reactions of Substituted Ammonium Cations.

Many substituted ammonium cations form sparingly soluble *picrates*, which are precipitated when picric acid[2] and the substituted ammonium salts are mixed in aqueous solution.

> To a solution of aniline hydrochloride (2 spatula-points) in water (1 ml.) add picric acid (saturated aqueous solution, 1 ml.). A yellow precipitate of aniline picrate is formed.

3. Reactions of Anions of Salts.

Substituted ammonium salts give the usual reactions of their anions, *e.g.*, Cl^-, SO_4^{--} in aqueous solution. Contrast compounds where the halogen and sulphate radicals are covalently linked to carbon (halides, p. 353; sulphuric acid esters, p. 430).

> Show that solutions of aniline hydrochloride and sulphate give the reactions of the chloride and sulphate ions (see pp. 260 and 252).

---

[1] pH range 3 (blue) to 5 (red).
[2] Picric acid is a phenol $C_6H_2(OH)(NO_2)_3$, in which the hydrogen of the hydroxyl radical is strongly acidic ($pK_a = 0.80$).

4. Inertness of Amines to Strong Alkalis.

While the salts of amines are decomposed by strong alkalis, the free amines being liberated, the latter are themselves *not* decomposed by alkali even on boiling. Contrast amides (pp. 350-351).

REACTIONS WHICH DISTINGUISH BETWEEN DIFFERENT TYPES OF AMINES

5. Acylation.

Primary and secondary amines on treatment with acyl chlorides or acid anhydrides give acyl derivatives (substituted amides), thus, *e.g.*,

$$R.NH_2+Cl.CO.R' = R.NH.CO.R'+HCl.$$
$$R.NH_2+O(CO.R')_2 = R.NH.CO.R'+HOOC.R'.$$
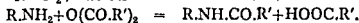
Tertiary amines do *not* form acyl derivatives.

> To aniline (10 drops) in a *dry* test-tube add acetic anhydride (10 drops). The mixture becomes hot. Heat it in a boiling water bath for 5 minutes and then pour it into water (20 ml.). (If an oil separates, scratch with a glass rod until it solidifies.) Filter the precipitated acetanilide by suction and recrystallise it from boiling water (m.p. 114°).

6. Condensation with Carbonyl Compounds.

Primary amines condense with carbonyl compounds to give products called Schiff's bases, as follows :

$$R'R''C:O+H_2N.R = R'R''C:N.R+H_2O.$$

This is an example of a general condensation reaction of carbonyl compounds considered on p. 330. (In some cases, further more complicated reactions follow the condensation.)

> Heat in a boiling water bath for 10 minutes benzaldehyde (20 drops) and aniline (20 drops). Cool, add ethyl alcohol (10 drops) and scratch with a glass-rod. The product (benzalaniline, $C_6H_5CH:N.C_6H_5$) crystallises as a white solid ; it may be recrystallised from ethyl alcohol (m.p. 48°).

7. Reactions with Nitrous Acid.

The nitrous acid in all these reactions is made on the spot from a solution of ⋯⋯⋯⋯⋯⋯⋯⋯⋯
$=HNO_2$.
acid decom⋯⋯⋯⋯⋯⋯⋯⋯⋯
NO_2+H_2O.

IONIC REACTIONS

1. Basic Properties.

For discussion of reactions see introduction to this section.

(a) Formation of Salts from Amines and Acids.

Carry out the following reaction with methylamine (approximately 2M aqueous solution, 5 ml.) and aniline (20 drops) in turn. Note that aniline, which the preliminary examination has shown to be sparingly soluble in water, is readily " soluble " in hydrochloric acid due to the formation of its hydrochloride.

> Take in a porcelain basin the amine, and add from a graduated pipette dilute hydrochloric acid until the mixture is just acid to Congo red paper.[1] Evaporate the solution to dryness on the boiling water bath. The amine hydrochloride remains as an odourless residue. Show that this gives the reactions of chloride ion.

(b) Displacement of Amines from their Salts by Strong Bases.

Carry out the following experiment with methylamine hydrochloride and aniline hydrochloride (prepared in (a)), and with ammonium chloride for comparison:

> Dissolve the salt (2 spatula-points) in water (2 ml.) and add sodium hydroxide (2 ml.). The amine (or ammonia) is liberated; aniline, being sparingly soluble in water, separates from solution; since methylamine and ammonia are soluble in water but volatile, they do not separate but their smell is perceptible.

(c) Determination of the Equivalent of an Amine.

See pp. 148-149.

2. Precipitation Reactions of Substituted Ammonium Cations.

Many substituted ammonium cations form sparingly soluble *picrates*, which are precipitated when picric acid[2] and the substituted ammonium salts are mixed in aqueous solution.

> To a solution of aniline hydrochloride (2 spatula-points) in water (1 ml.) add picric acid (saturated aqueous solution, 1 ml.). A yellow precipitate of aniline picrate is formed.

3. Reactions of Anions of Salts.

Substituted ammonium salts give the usual reactions of their anions, e.g., Cl⁻, SO₄⁻⁻ in aqueous solution. Contrast compounds where the linked to carbon (halides,

chloride and sulphate give the reactions of the chloride and sulphate ions (see pp. 260 and 252).

[1] pH range 3 (blue) to 5 (red).
[2] Picric acid is a phenol $C_6H_2(OH)(NO_2)_3$, in which the hydrogen of the hydroxyl radical is strongly acidic ($pK_a = 0.80$).

nitrogen being evolved (compare aliphatic primary amines, (a) above, and amides).

$$ArNH_2+HNO_2 = ArOH+N_2+H_2O.$$

The diazonium salts prepared as in (i) above decompose on heating to give the corresponding phenol and nitrogen.

$$ArN_2Cl+H_2O = ArOH+N_2+HCl.$$
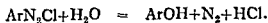
Prepare a solution of benzene diazonium chloride (as in reaction (i)). Warm the solution gently in a water-bath; gas is evolved and a dark oil (impure phenol) floats on the surface of the liquid (smell). When the evolution of gas has ceased, test the solution for phenol by Millon's reaction.

(c) Aliphatic or Aromatic Secondary Amines.

These react with nitrous acid to give nitrosamines, which are yellow liquids or solids.

$$RR'NH+HNO_2 = RR'N.N{:}O+H_2O.$$

The derivatives from lower aliphatic amines are soluble in water. Those from higher aliphatic and all aromatic amines are not.

To methylaniline (10 drops) add dilute hydrochloric acid (2 ml.). To the solution add gradually and with shaking sodium nitrite solution (2 ml.). A yellow oil (phenylmethylnitrosamine) separates.

(d) Aliphatic Tertiary Amines.

These do *not* react with nitrous acid except to give salts (amine nitrites).

(e) Aromatic Tertiary Amines.

Many of these react with nitrous acid at 0°, not however through the nitrogen atom of the amine group as do the primary and secondary amines, but in the para position of the aromatic nucleus. Dimethylaniline, for example, gives *p*-nitrosodimethylaniline :

$$C_6H_5.N.(CH_3)_2+HNO_2 = O{:}N.C_6H_4.N(CH_3)_2+H_2O.$$
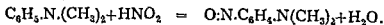
Dissolve dimethylaniline (5 drops) in dilute hydrochloric acid (2 ml.), cool in ice, and add dropwise, with constant shaking ice-cold sodium nitrite solution (1 ml.). The reddish-brown hydrochloride of the nitroso compound is precipitated. After the mixture has ⸱⸱⸱ ⸱ ⸱ ⸱ ⸱ ⸱ ⸱ ⸱ with sodium hydroxide sc⸱ ⸱ ⸱ ⸱ ⸱ ⸱ nges to green as the free b ⸱ ⸱ ⸱ ⸱ ⸱ ⸱ ⸱d.

(a) Aliphatic Primary Amines.

These react with nitrous acid to give directly the corresponding alcohol and nitrogen, both at temperatures *above* 5° and at temperatures *below* 5° (contrast aromatic primary amines (*b*), and compare amides, p. 351).

$$Alk.NH_2 + O:N.OH = Alk.OH + N_2 + H_2O.$$
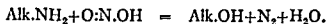
(i) To sodium nitrite solution (ice-cold, 2 ml.) add dilute acetic acid (ice-cold, 2 ml.). Shake and allow any effervescence (*oxides of nitrogen*) *to subside.* Then add the mixture to methylamine hydrochloride solution (2 ml.) and note the effervescence (nitrogen).

Primary amines in which the NH_2 radical is attached to an aromatic nucleus through a side-chain (*e.g.*, benzylamine) resemble aliphatic primary amines in their behaviour towards nitrous acid.

(ii) Repeat experiment (i), using a solution of benzylamine (3 drops) in dilute acetic acid (2 ml.) instead of methylamine hydrochloride.

(b) Aromatic Primary Amines.

(i) *In the Cold.* At temperatures *below* 5°, nitrous acid reacts with primary aromatic amines to give diazonium salts.

$$ArNH_3Cl + HNO_2 = ArN_2Cl + 2H_2O.$$

The diazonium salts (which are soluble in water) are very important because from them can be prepared many different types of simple aromatic compounds, and also dyestuffs by " coupling " with phenols and amines. Coupling generally takes place in the positions para or ortho to the position occupied by the phenolic or amino-group.

Benzene diazonium chloride (prepared from aniline and nitrous acid) couples with β-naphthol in alkaline solution to give benzene-azo-β-naphthol.

$$C_6H_5.N_2.Cl + C_{10}H_7OH = C_6H_5.N_2.C_{10}H_6.OH + HCl.$$
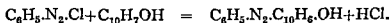
Dissolve aniline (3 drops) in dilute hydrochloric acid (5 ml.). Cool the solution in ice-water and add to it slowly and with shaking sodium nitrite solution (1 ml., previously cooled in ice-water). This gives a solution of benzene diazonium chloride.

In another tube dissolve β-naphthol (1 spatula-point) in dilute sodium hydroxide solution (10 ml.) and cool in ice-water. When the naphthol solution is cold, add to it the cold diazonium salt solution prepared as above. A brilliant red precipitate of benzene-azo-β-naphthol is formed.

(ii) *At Higher Temperatures.* At temperatures *above* 5°, nitrous acid and an aromatic primary amine give the corresponding phenol,

Ammonium Salt.

(c) ... .

Amine.

(d) Repeat (a), using aniline (5 drops) instead of acetamide. On boiling the mixture smells of aniline, *not* of ammonia.

2. Hydrolysis by Acid.

Amides are hydrolysed by mineral acids, giving the corresponding carboxylic acid and the ammonium salt of the mineral acid.

$$R.CONH_2 + H_2O + H^+ = R.COOH + NH_4^+.$$
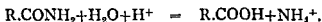
Boil acetamide (2 spatula-points) with dilute hydrochloric acid (5 ml.) for two minutes. Acetic acid and ammonium chloride are formed (the former can be recognised by its smell in the escaping steam). Cool the mixture thoroughly and make alkaline with sodium hydroxide solution. Ammonia is evolved in the cold.

3. Reaction with Nitrous Acid.

Amides react with nitrous acid, giving the corresponding carboxylic acid, nitrogen and water. (Compare aliphatic primary amines, p. 348.)

$$R.CONH_2 + O:NOH = R.COOH + N_2 + H_2O.$$

Prepare a solution of nitrous acid by adding dilute hydrochloric acid (ice-cold, 1 ml.) to sodium nitrite solution (ice-cold, 1 ml.). Allow the effervescence which occurs on mixing to cease, and immediately add the mixture to a solution of acetamide (1 spatula-point in 2 ml. water). A further effervescence takes place, nitrogen being evolved.

12, 14   THE NITRO RADICAL

Radical: $-N \begin{smallmatrix} O \\ \nearrow \\ \searrow \\ O \end{smallmatrix}$ or NO_2.

Class of compounds:

Nitro compounds (Aromatic), Ar$-N \begin{smallmatrix} O \\ \nearrow \\ \searrow \\ O \end{smallmatrix}$ or Ar.NO_2.
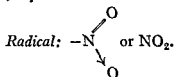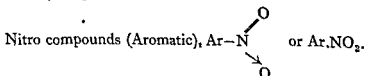
Aromatic nitro compounds alone are considered here. Aliphatic nitro compounds can be prepared, but are much less important. In simple compounds the nitro radical is neither acidic nor basic in

12, 13   THE AMIDE RADICAL

Radical: $-\overset{\overset{\textstyle O}{\|}}{C}$ or $-CONH_2$.

Class of compounds: Amides, $R.\overset{\overset{\textstyle O}{\|}}{C}$ or $R.CONH_2$.
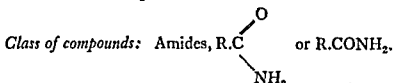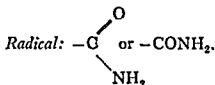
The amides are *neutral* substances (contrast amines). The amide radical is water-attractive; the solubilities of the amides in water follow the same rules as those of carboxylic acids or alcohols.

For reactions of a substituted amide, acetanilide, $C_6H_5.NH.CO.CH_3$, see p. 431.

REPRESENTATIVE COMPOUNDS

Compound	m.p.	b.p.	d (g. per ml.)	s in water (g. per 100 ml.)
Acetamide $CH_3.CONH_2$	81°	222°	1·16	98
Benzamide $C_6H_5.CONH_2$	130°	290°	1·34	1

REACTIONS

1. Hydrolysis by Alkali.

Amides are hydrolysed by caustic alkalis *on boiling*, giving ammonia and the alkali salt of the corresponding acid.

$$R.CONH_2 + OH^- = R.COO^- + NH_3\uparrow.$$

Amides are *not* affected by caustic alkalis at room temperature (contrast ammonium salts). Amines are *not* affected by caustic alkalis even on boiling.

Amides.

(*a*) Take in a boiling-tube acetamide (2 spatula-points), add sodium hydroxide solution (5 ml.), shake, allow to stand for a minute and smell. No smell of ammonia is perceptible. Now boil the mixture; ammonia is evolved (smell and test with litmus paper). Continue boiling until no more ammonia is given off. Cool and acidify with dilute hydrochloric acid. The smell of acetic acid is perceptible.

(*b*) Repeat (*a*), using benzamide (2 spatula-points) instead of acetamide. On acidifying the final solution benzoic acid is precipitated.

THE HALIDE RADICAL

Radical: —Hal (—Cl, —Br or —I).

Classes of compounds: Alkyl Halides, Alk.Hal ; Aryl Halides, Ar.Hal.

The halide radical does *not* ionise (contrast metallic halides) and is *not* water-attractive. The alkyl and aryl halides are neutral compounds, sparingly soluble in water.

The alkyl halides (and aromatic halogen compounds containing halogen in the side chain, *e.g.,* benzyl chloride, $C_6H_5.CH_2.Cl$) are reactive compounds. By treatment with the appropriate reagents (sodium hydroxide, sodium alkoxide, potassium cyanide, silver acetate, etc.) the halogen atom can be readily replaced by various radicals (hydroxyl, alkoxyl, cyanide, acetate, etc.).

In the aryl halides—*i.e.,* compounds in which halogen is *directly* attached to an aromatic nucleus (*e.g.,* chlorobenzene, $C_6H_5.Cl$)—the halogen atom is unreactive and does not usually undergo the double decomposition reactions with sodium hydroxide, sodium alkoxide, etc.

REPRESENTATIVE COMPOUNDS

Compound	m.p.	b.p.	d (g. per ml.)	s in water (g. per 100 ml.)
Ethyl chloride $C_2H_5.Cl$	$-139°$	$12°$	0·92	0·6
Ethyl bromide $C_2H_5.Br$	$-119°$	$38°$	1·43	0·9
Ethyl iodide $C_2H_5.I$	$-108°$	$72°$	1·93	0·4
n-Amyl chloride $C_5H_{11}.Cl$	$-99°$	$108°$	0·88	n
Benzyl chloride $C_6H_5.CH_2.Cl$	$-43°$	$179°$	1·10	n
Chlorobenzene $C_6H_5.Cl$	$-45°$	$132°$	1·11	0·05

REACTIONS

1. Covalent Linkage of Halogen.

The halogen in alkyl halides is covalently linked to carbon and therefore does *not* give the reactions of the halide ions.

(*a*) Shake *n*-amyl chloride (5 drops) with aqueous silver nitrate solution (2 ml.). No precipitate is formed.

(*b*) and (*c*). Repeat (*a*), using benzyl chloride and chlorobenzene instead of *n*-amyl chloride.

2. Hydrolysis by Alkali.

The halogen in all halides, *except* those in which it is directly attached

character.[1] It is not water-attractive. The nitro compounds are therefore neutral and very sparingly soluble in water. Most nitro compounds are yellow.

<div align="center">REPRESENTATIVE COMPOUND</div>

Compound	m.p.	b.p.	d (g. per ml.)	s in water (g. per 100 ml.)
Nitrobenzene* $C_6H_5.NO_2$	6°	211°	1·20	0·2

<div align="center">* Yellow.</div>

<div align="center">REACTIONS</div>

1. Reduction.

Nitro compounds are reduced by different reducing agents to different products. Treatment with tin and hydrochloric acid (*i.e.*, with nascent hydrogen in acidic solution) yields primary amines.

$$ArNO_2 + 6(H) = ArNH_2 + 2H_2O.$$

Take in a boiling-tube nitrobenzene (1 ml.), concentrated hydrochloric acid (5 ml.) and granulated tin (two pieces), and *heat the mixture with shaking in the boiling water bath until oily drops are no longer visible.* (If the initial reaction between the tin and hydrochloric acid is vigorous, remove the tube from the bath until the reaction subsides.) Decant the liquid from undissolved tin into a conical flask, cool thoroughly under the tap, and add carefully aqueous sodium hydroxide solution (20%) until the precipitate which forms is re-dissolved. Pour the mixture, which now smells of aniline, into a separating funnel, add ether (10 ml.) (keep as far away from flames as possible), shake thoroughly and separate the two layers. Wash the ether layer with water (5 ml.) and again separate the layers. Run the ether layer into a dry test-tube, add anhydrous calcium chloride (a few small pieces) and shake until the liquid is clear. Filter the liquid into a dry test-tube, and evaporate the ether by warming the mixture gently with shaking in a *previously warmed water bath as far away from flames as possible.* When all the ether has evaporated a yellow liquid (impure aniline, about 1 ml.) remains in the tube. Note its smell, dissolve it in *dilute hydrochloric acid, diazotise it* and couple it with β-naphthol (see p. 348).

(The nitration of nitrobenzene, which is a reaction of the aromatic nucleus, is described on p. 319.)

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[1] The changes in colour which take place when polynitro compounds are treated with alkali are due to the formation of salts by a tautomeric form of the nitro radical, which is acidic.

THE HALIDE RADICAL

Radical: —Hal (—Cl, —Br or —I).

Classes of compounds: Alkyl Halides, Alk.Hal; Aryl Halides, Ar.Hal.

The halide radical does *not* ionise (contrast metallic halides) and is *not* water-attractive. The alkyl and aryl halides are neutral compounds, sparingly soluble in water.

The alkyl halides (and aromatic halogen compounds containing halogen in the side chain, *e.g.*, benzyl chloride, $C_6H_5.CH_2.Cl$) are reactive compounds. By treatment with the appropriate reagents (sodium hydroxide, sodium alkoxide, potassium cyanide, silver acetate, etc.) the halogen atom can be readily replaced by various radicals (hydroxyl, alkoxyl, cyanide, acetate, etc.).

In the aryl halides—*i.e.*, compounds in which halogen is *directly* attached to an aromatic nucleus (*e.g.*, chlorobenzene, $C_6H_5.Cl$)—the halogen atom is unreactive and does not usually undergo the double decomposition reactions with sodium hydroxide, sodium alkoxide, etc.

REPRESENTATIVE COMPOUNDS

Compound	m.p.	b.p.	d (g. per ml.)	s in water (g. per 100 ml.)
Ethyl chloride $C_2H_5.Cl$	—139°	12°	0·92	0·6
Ethyl bromide $C_2H_5.Br$	—119°	38°	1·43	0·9
Ethyl iodide $C_2H_5.I$	—108°	72°	1·93	0·4
n-Amyl chloride $C_5H_{11}.Cl$	—99°	108°	0·88	n
Benzyl chloride $C_6H_5.CH_2.Cl$	—43°	179°	1·10	n
Chlorobenzene $C_6H_5.Cl$	—45°	132°	1·11	0·05

REACTIONS

1. Covalent Linkage of Halogen.

The halogen in alkyl halides is covalently linked to carbon and therefore does *not* give the reactions of the halide ions.

(*a*) Shake *n*-amyl chloride (5 drops) with aqueous silver nitrate solution (2 ml.). No precipitate is formed.

(*b*) and (*c*). Repeat (*a*), using benzyl chloride and chlorobenzene instead of *n*-amyl chloride.

2. Hydrolysis by Alkali.

The halogen in all halides, *except* those in which it is directly attached

to an aromatic nucleus, is replaced by hydroxyl on boiling with dilute aqueous alkali. The solution then gives the reactions of the halide ion.

$$·Alk.Hal + OH^- \rightleftharpoons Alk.OH + Hal^-.$$

Halides in which the halogen is directly attached to an aromatic nucleus are not affected by this treatment.

nitric acid, and to the resulting solution (2 ml.) add silver nitrate solution. A white precipitate of silver chloride is formed.

(b) Repeat (a), using benzyl chloride instead of n-amyl chloride. The same result is obtained.

(c) Repeat (a), using chlorobenzene instead of n-amyl chloride. No precipitate of silver chloride is formed.

12, 16   THE SULPHONIC ACID RADICAL

$$Radical:\ \begin{array}{c} O \\ \uparrow \\ -S-OH \\ \downarrow \\ O \end{array} \text{ or } -SO_3H.$$

Class of compounds: Sulphonic Acids (Aromatic),

$$\begin{array}{c} O \\ \uparrow \\ Ar-S-O-H \\ \downarrow \\ O \end{array} \text{ or } Ar.SO_3H, \text{ and their salts.}$$

Aromatic sulphonic acids alone are considered here. Aliphatic sulphonic acids can be prepared, but are much less important.

The hydrogen of the sulphonic acid radical ionises almost completely in aqueous solution ; $Ar.SO_3H \rightleftharpoons Ar.SO_3^- + H^+$. The sulphonic acids are therefore strong acids, and cannot be displaced from their salts by other acids (contrast carboxylic acids). The radical is strongly water-attractive, and the acids are therefore readily soluble in water.

The salts of the sulphonic acids are also strong electrolytes, many of them (including the ammonium, alkali metal and alkaline earth metal salts) being soluble in water.

The acids are not hydrolysed by boiling with dilute acids (contrast sulphuric acid esters, p. 430). They are, however, decomposed by fusion with caustic alkali (see reaction 6). The sulphonic acids are esterified by treatment of the acyl chloride (not the acid itself) with a hydroxy compound. The esters are of little importance.

REPRESENTATIVE COMPOUNDS

Compound	m.p.	b.p.	d (g. per ml.)	s in water (g. per 100 ml.)
Benzenesulphonic acid $C_6H_5.SO_3H$	44°	137°		v
p-Toluenesulphonic acid $p.CH_3C_6H_4.SO_3H$	107°	140° (20 mm)		v

The sodium salts of these acids are solids, non-volatile and readily soluble in water.

REACTIONS

IONIC REACTIONS

1. **Acidic Properties.**

For discussion of reactions see introduction to this section.

(a) *Formation of Salt from Acid and Base.*

To p-toluenesulphonic acid (approximately 2M aqueous solution, 5 ml.) add sodium hydroxide solution (approximately 2M) until the mixture is neutral to litmus-paper. Evaporate the solution to dryness on the boiling water bath. Sodium p-toluene-sulphonate is left as a white crystalline solid.

(b) *Formation of Salt from Acid by Displacement of a Weaker Acid (Carbonic Acid).*

To p-toluenesulphonic acid (1 spatula-point) add sodium bicarbonate solution (2 ml.). Effervescence occurs, carbon dioxide being evolved.

(c) *Comparison of Strength of Sulphonic, Carboxylic and Mineral Acid.*

The strengths of p-toluenesulphonic, acetic, and hydrochloric acid can be compared by determining approximately the pH values of 0·1M sol   -165).
At this   cid of
pK_a approximately 5 (*e.g.*, acetic) has a pH of approximately 3.

To 2 ml. of the given 0·1M solutions of each of the acids (p-toluenesulphonic, acetic, hydrochloric) add methyl violet indicator (1 drop) and shake. Note that the pH of the sulphonic acid solution is approximately the same as that of hydrochloric acid solution.

to an aromatic nucleus, is replaced by hydroxyl on boiling with dilute aqueous alkali. The solution then gives the reactions of the halide ion.

$$\cdot Alk.Hal + OH^- \rightleftharpoons Alk.OH + Hal^-.$$

Halides in which the halogen is directly attached to an aromatic nucleus are not affected by this treatment.

(a) Heat · · · · · · · · · · · · · · · · · · · · · · · · · · · · · ·
solution, 5
· · ·

· nitrate

(b) Repeat (a), using benzyl chloride instead of n-amyl chloride. The same result is obtained.

(c) Repeat (a), using chlorobenzene instead of n-amyl chloride. No precipitate of silver chloride is formed.

12, 16   THE SULPHONIC ACID RADICAL

$$Radical: \quad -\overset{\overset{\displaystyle O}{\uparrow}}{\underset{\downarrow}{\underset{\displaystyle O}{S}}}-OH \quad or \quad -SO_3H.$$

Class of compounds: Sulphonic Acids (Aromatic),

$$Ar-\overset{\overset{\displaystyle O}{\uparrow}}{\underset{\downarrow}{\underset{\displaystyle O}{S}}}-O-H \quad or \quad Ar.SO_3H, \text{ and their salts.}$$

Aromatic sulphonic acids alone are considered here. Aliphatic sulphonic acids can be prepared, but are much less important.

The hydrogen of the sulphonic acid radical ionises almost completely in aqueous solution; $Ar.SO_3H = Ar.SO_3^- + H^+$. The sulphonic acids are therefore *strong* acids, and cannot be displaced from their salts by other acids (contrast carboxylic acids). The radical is strongly water-attractive, and the acids are therefore readily soluble in water.

The salts of the sulphonic acids are also strong electrolytes, many of them (including the ammonium, alkali metal and alkaline earth metal salts) being soluble in water.

The acids are not hydrolysed by boiling with dilute acids (contrast sulphuric acid esters, p. 430). They are, however, decomposed by fusion with caustic alkali (see reaction 6). The sulphonic acids are esterified by treatment of the acyl chloride (not the acid itself) with a hydroxy compound. The esters are of little importance.

formed from the sulphite. Finally add to the warm solution Millon's reagent (1 ml.). A red colour is produced, due to the presence of a phenol.

12, 17   THE SULPHONAMIDE RADICAL

$$
\textit{Radical:} \quad -\overset{\overset{O}{\uparrow}}{\underset{\downarrow}{S}}-NH_2 \quad \text{or} \quad -SO_2.NH_2.
$$
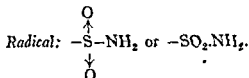
Class of compounds: Sulphonamides (Aromatic),

$$
Ar-\overset{\overset{O}{\uparrow}}{\underset{\downarrow}{S}}-NH_2, \quad Ar.SO_2.NH_2.
$$
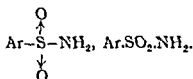
The sulphonamides are *very* weak acids (contrast amides of carboxylic acids, which are neutral), one hydrogen atom of the sulphonamide radical being replaceable by metals thus:

$$Ar.SO_2.NH_2 + OH^- = Ar.SO_2.NH^- + HOH.$$

The compounds are so weakly acidic that they do *not* redden litmus.

The sulphonamide radical is moderately water-attractive; aryl sulphonamides are therefore sparingly soluble in water (compare solubilities of benzamide and benzenesulphonamide). The sodium derivatives of the sulphonamides are readily soluble in water; sulphonamides which are insoluble in water therefore " dissolve " in dilute caustic alkali; they are precipitated on the addition of mineral acid or carboxylic acid, or on passing carbon dioxide into the solution.

$$Ar.SO_2.NH^- + H^+ = Ar.SO_2.NH_2.$$
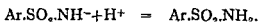
REPRESENTATIVE COMPOUNDS

Compound	m.p.	b.p.	d (g. per ml.)	s in water (g. per 100 ml.)
Benzenesulphonamide $C_6H_5.SO_2.NH_2$	156°			0·4
p-Toluenesulphonamide p-$CH_3.C_6H_4.SO_2.NH_2$	137°			1·9

2. Reactions of Sulphonate Anions.

The barium salts of many sulphonic acids are soluble in water (some only on boiling). This solubility serves to distinguish and to separate the acids from sulphuric acid.

> To p-toluenesulphonic acid (2M solution, 1 ml.) add barium nitrate solution (5 drops). *No* precipitate is formed.

3. Reactions of Cations of Salts.

Sulphonates give the usual reactions of their cations in solution. The liberation of ammonia by *cold* caustic alkali from ammonium sulphonates is valuable in distinguishing these from sulphonamides.

OTHER REACTIONS

4. Reaction with Phosphorus Pentachloride.

Sulphonic acids like carboxylic acids react with phosphorus pentachloride on warming to give the acyl chlorides (sulphonyl chlorides).

$$Ar.SO_2.OH + PCl_5 = Ar.SO_2.Cl + POCl_3 + HCl\uparrow.$$
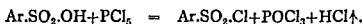
The sulphonyl chlorides are solids, insoluble in and not readily decomposed by water. They are valuable as intermediates for the preparation of sulphonamides and sulphonic esters.

> Mix phosphorus pentachloride and p-toluenesulphonic acid ($\frac{1}{4}$ spatula-point each) in an ignition tube. Warm gently until no more hydrogen chloride is evolved. Cool and add water (10 drops). The sulphonyl chloride separates as an oil which solidifies on scratching.

5. Inertness towards Hydrolysis.

The C–S link in sulphonic acids is *not* hydrolysed by boiling the substances with mineral acids (contrast the O–S link in esters of sulphuric acid, and see comparative experiment, p. 430).

6. Decomposition by Alkali Fusion.

Aryl sulphonic acids or their salts are decomposed by fusion with *caustic alkalis*, giving a phenol and alkali sulphite.

$$Ar.SO_3Na + NaOH = Ar.OH + Na_2SO_3.$$

> To p-toluenesulphonic acid (1 spatula-point) in a hard-glass ignition tube add sodium hydroxide (2 pellets), heat until the mixture fuses and continue heating for a minute. Allow to cool, add water (2 ml.) and warm gently to dissolve the solid reaction products. Acidify with dilute sulphuric acid ; note the phenolic smell. Warm and note the smell of sulphur dioxide, which is

CLASSIFICATION OF SIMPLE ORGANIC COMPOUNDS

13, 1 INTRODUCTION

SCOPE OF WORK

This chapter deals with the classification, but not the identification, of single organic compounds containing not more than one substituent radical selected from the classes listed below.

The method of classification outlined here involves a systematic study of the reactions of the unknown compound. It must *not* be followed blindly and rigidly, but applied with common-sense and with the student's general knowledge of organic chemistry.

The method enables the student to deduce what substituent radical (if any) is present in a compound (*i.e.*, to what *class* the compound belongs); it may enable him to say whether the compound is aliphatic or aromatic, and whether an aliphatic compound is a lower, middle or higher member of its class. It does *not* enable him to *identify* any unknown compound. The fact that an unknown substance reacts as, *e.g.*, a primary aromatic amine and appears on superficial examination to be aniline, unless the student has handled, does not justify him in saying that it is aniline.

The nature of the work required for the *identification* of an organic compound—measurement of physical properties and comparison with known substances—has been mentioned in Chapter 11 (pp. 302-303). Details if required must be obtained from other books.

For methods of classifying and identifying compounds not covered in this chapter, and for methods of separating mixtures, other books must be consulted.

CLASSES OF COMPOUNDS

The method covers the following classes of compounds:

1. Containing Carbon, Hydrogen, (Oxygen).

Aliphatic hydrocarbons (paraffins)	Ethers
,, ,, (olefins)	Aldehydes
Aromatic hydrocarbons	Ketones
Alcohols	Carboxylic acids
Phenols	Esters

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REACTIONS

IONIC REACTIONS

1. Acidic Properties.

For discussion of reactions see the introduction to this section.

To *p*-toluenesulphonamide (1 spatula-point) add sodium hydroxide solution (2 ml.). The sulphonamide "dissolves," due to the formation of its sodium derivative. Acidify with dilute hydrochloric acid; the sulphonamide is precipitated.

OTHER REACTIONS

2. Hydrolysis.

The sulphonamides are hydrolysed slowly by boiling mineral acids but not by boiling alkalis (contrast amides of carboxylic acids, p. 350). The reaction is not convenient for use here.

FURTHER READING

See the list of books on pp. 307-308.

CLASSIFICATION OF SIMPLE ORGANIC COMPOUNDS

13, 1   INTRODUCTION

SCOPE OF WORK

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The method of classification outlined here involves a systematic study of the reactions of the unknown compound. It must *not* be followed blindly and rigidly, but applied with common-sense and with the student's general knowledge of organic chemistry.

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1. Containing Carbon, Hydrogen, (Oxygen).

Aliphatic hydrocarbons (paraffins)	Ethers
" " (olefins)	Aldehydes
Aromatic hydrocarbons	Ketones
Alcohols	Carboxylic acids
Phenols	Esters

13, 2   **REPORTS**

The reason for applying each test, the nature of the test, the results and the conclusions drawn from them must be written in a note-book *immediately* the test has been done. It must be realised that negative evidence—the fact that a substance gives *no* visible change with a certain reagent—is just as important as positive evidence.

The following form of report is suggested :

24 May 1945.   Examination of Substance No. 14

Reason for Test	Test [1]	Observation	Conclusion [2]
Preliminary examination.	Appearance of substance.	Colourless liquid.	
	Smell of substance.	Like ethyl alcohol.[2]	Substance may be lower alcohol.
Tests for elements.	Substance burnt on porcelain.	No residue. (Flame *not* smoky.)	Metals absent. (Substance probably aliphatic.)
	Sodium-fusion test applied to substance.		
	Filtrate tested		
	(*a*) for nitrogen,	No blue colour or ppt.	Nitrogen absent.
	(*b*) for halogens,	No ppt.	Halogen absent.
	(*c*) for sulphur.	No brown colour or ppt.	Sulphur absent, *i.e.*, substance contains CH(?O).
Tests for radicals. Classification tests.	Substance (4 drops) +water (2 ml.).	Substance soluble.	
	Aqueous solution of substance tested with litmus.	Neutral.	Substance not acid or phenol.
	Substance + aqueous DNPH reagent.	No ppt.	Substance not aldehyde or ketone.
	Substance+PCl₅.	Vigorous reaction.	Substance is an ALCOHOL.
Further tests.	Substance+acetic anhydride.	Water-insoluble fruity-smelling product formed.	Alcohol confirmed.
	Substance+ sodium.	Vigorous effervescence.	Alcohol confirmed.
	Substance+potassium dichromate+conc. H₂SO₄.	Dichromate reduced to green chromic salt, smell of aldehyde.	Substance is a PRIMARY or SECONDARY alcohol.
	Miscibility of substance with water tested over whole range.	Substance miscible with water in all proportions.	Substance is a LOWER alcohol.

Conclusion[3]: Substance No. 14 is an ALCOHOL (LOWER ALIPHATIC, PRIMARY or SECONDARY).[4]

Points to Note.

1. The material used for a test (" substance," " aqueous solution of substance ") is always stated.

2. A sharp distinction is drawn between *certainties* (" metals absent ") and *possibilities* or *probabilities* (" probably aliphatic ").

3. The final *conclusion* is stated *boldly*.

4. The facts that the substance reacts as a lower primary or secondary aliphatic alcohol and smells *like* ethyl alcohol do *not* justify the assumption that it *is* ethyl alcohol.

13, 3   PRELIMINARY EXAMINATION

Note the appearance (state, colour, etc.) and the smell of the substance. These properties may give useful clues as to the nature of the substance. Do *not* allow first impressions to prejudice your interpretation of later results.

TESTS FOR ELEMENTS

13, 4   IGNITION TEST FOR METALS

If an organic compound containing a metal is ignited, the organic part of the molecule is burnt away and a non-volatile residue of the oxide, carbonate or sulphate of the metal is left. This residue may be tested for cations in the usual way (see Chapter 10, pp. 286–292). If an organic compound *not* containing a metal is ignited, it is burnt completely and no residue is left. (Heating to a bright red-heat for a minute may be necessary to burn away the carbon obtained from some compounds.)

The main purpose of the ignition test is to detect the presence of metals. Other useful information may be obtained incidentally by noting the way in which the substance burns, and the smell of vapours evolved. A smoky flame usually but not invariably indicates an aromatic compound.

Take the substance (if solid, 1 spatula-point; if liquid, 2–3 drops) on a piece of porcelain or a nickel spatula and lower it slowly into the Bunsen flame. Note how the substance burns and the smell of any vapours produced. Continue to heat until no further change takes place; if a residue remains, heat to bright red-heat for a minute before assuming that it is not combustible.

13, 2   **REPORTS**

The reason for applying each test, the nature of the test, the results
and the conclusions drawn from them must be written in a note-book
immediately the test has been done. It must be realised that negative
evidence—the fact that a substance gives *no* visible change with a
certain reagent—is just as important as positive evidence.

The following form of report is suggested :

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	Sodium-fusion test applied to substance. Filtrate tested		
	(a) for nitrogen,	No blue colour or ppt.	Nitrogen absent.
	(b) for halogens,	No ppt.	Halogen absent.
	(c) for sulphur.	No brown colour or ppt.	Sulphur absent, *i.e.*, substance contains CH(?O).
Tests for radicals. Classification tests.	Substance (4 drops) +water (2 ml.).	Substance soluble.	
	Aqueous solution of substance tested with litmus.	Neutral.	Substance not acid or phenol.
	Substance + aqueous DNPH reagent.	No ppt.	Substance not aldehyde or ketone.
	Substance+PCl₅.	Vigorous reaction.	Substance is an ALCOHOL.
Further tests.	Substance+acetic anhydride.	Water-insoluble fruity-smelling product formed.	Alcohol confirmed.
—	Substance+ sodium.	Vigorous effervescence.	Alcohol confirmed.
	Substance+potassium dichromate+ conc. H₂SO₄.	Dichromate reduced to green chromic salt, smell of aldehyde.	Substance is a PRIMARY or SECONDARY alcohol.
	Miscibility of substance with water tested over whole range.	Substance miscible with water in all proportions.	Substance is a LOWER alcohol.

THE SODIUM FUSION

Before starting the fusion, put distilled water (10 ml.) in a porcelain basin on your bench. Take in a soft-glass tube ($3'' \times \frac{1}{4}''$) a small piece of clean sodium [1] and warm the tube gently in a small Bunsen flame until the sodium melts and runs to the bottom of the tube. Remove the tube from the flame and add the organic compound (if solid, use $\frac{1}{2}$ spatula-point; if liquid,[2] use 2 drops).

Hold the tube with forceps in the right hand, and hold a piece of wire gauze in the left hand between your face and the tube in case the reaction with sodium is violent. Now heat the tube gently at first, then to a red-heat until no further visible change occurs. While the tube is still red-hot plunge it into the water in the porcelain basin, holding the wire gauze over the basin to prevent spurting. Crush the fragments of tube and contents with a glass rod and filter. Divide the filtrate, which should be clear and colourless, into four parts (I, II, III, IV). (If the filtrate is not clear and colourless, repeat the fusion, using the same quantity of compound as before with *twice* the quantity of sodium previously used. Heat very slowly and thoroughly.)

THE DETECTION OF NITROGEN

To the sodium-fusion filtrate (Part I) add a small crystal of ferrous sulphate. (A greenish-grey precipitate of impure ferrous hydroxide is formed in all cases. If sulphur was present in the original substance, the precipitate is black, owing to the formation of ferrous sulphide.) Boil the mixture gently for a minute to ensure the formation of ferrocyanide, if any nitrogen is present, and then cool under the tap. Add ferric chloride solution (2 drops) and then acidify with concentrated hydrochloric acid. A green or blue colour or blue precipitate of Prussian blue indicates the presence of nitrogen in the compound. This precipitate may best be seen by allowing the tube to stand for ten minutes and filtering.

THE DETECTION OF SULPHUR

To the sodium-fusion filtrate (Part II) add sodium plumbite solution (2 drops). A brown or black colour or precipitate (lead sulphide) indicates the presence of sulphur in the compound.

THE DETECTION OF HALOGENS

The procedure depends upon whether the compound has been found to contain nitrogen and/or sulphur, or not.

[1] The author's practice is to provide students with pieces of sodium wire removed (about one inch long). Th...

[2] It is practice i
unknown
informati

Practise using known Substances.

Carry out the ignition tests with the under-mentioned substances, noting all results. Where a residue is left, test this for the metal.

Stearic acid   (aliphatic, *not* containing metal).
Naphthalene   (aromatic, *not* containing metal).
Potassium tartrate (aliphatic, containing metal).
Calcium benzoate   (aromatic, containing metal).
Tartaric acid   (aliphatic, *not* containing metal—residue diffi-
                    cult to burn away).

13, 5   SODIUM-FUSION TEST FOR NITROGEN, SULPHUR AND HALOGENS

When an organic compound containing nitrogen, sulphur or halogen is heated strongly with metallic sodium the following reactions take place:

1. $Na+C+N$ (if any, in organic compound) $\rightarrow NaCN$, sodium cyanide.

2. $Na+S$ (if any, in organic compound) $\rightarrow Na_2S$, sodium sulphide.

3. $Na+Hal$ (if any, in organic compound) $\rightarrow NaHal$, sodium halide.

The following reaction takes place with *every* organic compound, whether or not nitrogen, sulphur or halogens are present:

4. Na (excess) $+O_2+H_2O+CO_2$ (from air and organic compound) $\rightarrow NaOH+Na_2CO_3$ (sodium hydroxide and carbonate).

If the reaction product is dissolved in water, the resulting solution may be tested for cyanide, sulphide and halide *ions* by the ordinary methods (see Chapter 9, pp. 217-219, 249, and 260-266).

The methods usually employed are as follows:

1. For cyanide (*i.e.*, for *nitrogen* in the original substance), formation of Prussian blue

$$6CN^-+Fe^{++} = [Fe(CN)_6]^{----} \text{ (ferrocyanide)}$$
$$[Fe(CN)_6]^{----}+Fe^{+++}+K^+ = KFe[Fe(CN)_6]\downarrow \text{(Prussian blue)}.$$

2. For sulphide (*i.e.*, for *sulphur* in the original substance), formation of lead sulphide

$$Pb^{++}+S^{--} = PbS\downarrow.$$
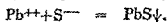
3. For halide (*i.e.*, for *halogen* in the original substance), formation of silver halide

$$Ag^++Hal^- = AgHal\downarrow.$$
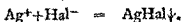
The halides are differentiated by the test with chlorine water and carbon tetrachloride.

Two points must be noted. First, the solution of the sodium-fusion product always contains much sodium hydroxide and carbonate. Secondly, the silver test for halide cannot be carried out on this solution until any cyanide and/or sulphide have been destroyed, since these ions if present will give precipitates of white silver cyanide and/or black silver sulphide.

CLASSIFICATION TESTS

TABLE 13, 7, A

Test solubility of substance in water

Soluble

**Alcohols, Phenols,
Ethers, Aldehydes,
Ketones,
Acids, Esters**

Insoluble

All Classes
See Table 13, 7, B

Test solution with litmus

Neutral

**Alcohols, Ethers,
Aldehydes, Ketones,
Esters**

Acidic

Phenols, Acids

Test substance with aqueous
DNPH [1] reagent

Precipitate [2]

Aldehydes, Ketones

No precipitate [2]

**Alcohols,
Ethers, Esters**
See Table 13, 7, C

Test substance with
Fehling's solution

Reduction

Aldehydes

No reduction

Ketones

Test substance with NaHCO₃

Effervescence

Acids

No effervescence

Phenols

[1] DNPH=Dinitrophenylhydrazine (see p. 331).
[2] Aldehydes or ketones give an immediate heavy precipitate. Alcohols contaminated with a trace of aldehyde or ketone give a faint precipitate on standing.

(1) *Nitrogen and Sulphur being Absent.* The sodium-fusion filtrate (Part III) is acidified with dilute nitric acid, and silver nitrate solution is then added. A white or yellow precipitate indicates the presence of halogen.

(2) *Nitrogen and/or Sulphur being Present.* The sodium-fusion filtrate (Part III) is made just acid to litmus by the addition of dilute nitric acid in an evaporating basin, water (5 ml.) is added, and the mixture is evaporated (*Fume Cupboard*) to half its volume. The solution is then cooled and tested for halides, as in (1) above, by the addition of nitric acid and silver nitrate solution.

DISTINCTION BETWEEN CHLORINE, BROMINE, AND IODINE

If halogen has been detected by the silver nitrate test, the sodium-fusion filtrate (Part IV) is acidified with dilute sulphuric acid, and carbon tetrachloride (2 ml.) is added. A few drops of chlorine water are then added, and the mixture is well shaken. The colour of the lower (carbon tetrachloride) layer indicates which halogen is present :

Violet	lower layer indicates iodine.
Brown	,,	,,	,,	bromine.
Colourless	,,	,,	,,	chlorine.

PRACTISE USING KNOWN SUBSTANCES

Before using the sodium-fusion test for the detection of elements in unknown substances the student should carry out the tests on known substan̶ ... ...) S (chloroacetamide).
... ... Hal (thiourea).
Substance containing *no* N, Hal or S (benzoic acid).

It is most important that those tests where a *negative* result is expected should be carried out—*e.g.*, the test for halogen on thiourea.

TESTS FOR RADICALS

13, 6   ### GENERAL INSTRUCTIONS

Tests should be carried out in the manner and with the quantities used when studying the reactions of radicals—*i.e.*, as detailed in Chapter 12 (pp. 312-358).

Tests for solubility in dilute hydrochloric acid and dilute sodium hydroxide should be carried out as follows:

If the unknown substance is a *solid*, test as for solubility in water (see p. 312).

If the unknown substance is a *liquid*, add it (4 drops, *i.e.*, about 0·2 ml.) to the solvent (2 ml.) in a test-tube and shake vigorously.

13, 7   ### SUBSTANCES CONTAINING C, H, (O)

Classes of Substances—Hydrocarbons (paraffin, olefin, aromatic), alcohols, phenols, ethers, aldehydes, ketones, carboxylic acids, esters.

CLASSIFICATION TESTS

TABLE 13, 7, A

Test solubility of substance in water

Soluble	**Insoluble**
Alcohols, Phenols, Ethers, Aldehydes, Ketones, Acids, Esters	**All Classes** See Table 13, 7, B

Test solution with litmus

Neutral	Acidic
Alcohols, Ethers, Aldehydes, Ketones, Esters	**Phenols, Acids**

Test substance with aqueous DNPH[1] reagent

Precipitate[2]	No precipitate[2]
Aldehydes, Ketones	**Alcohols, Ethers, Esters** See Table 13, 7, C

Test substance with Fehling's solution

Reduction	No reduction
Aldehydes	**Ketones**

Test substance with NaHCO₃

Effervescence	No effervescence
Acids	**Phenols**

[1] DNPH = Dinitrophenylhydrazine (see p. 331).
[2] Aldehydes or ketones give an immediate heavy precipitate. Alcohols contaminated with a trace of aldehyde or ketone give a faint precipitate on standing.

(1) *Nitrogen and Sulphur being Absent.* The sodium-fusion filtrate (Part III) is acidified with dilute nitric acid, and silver nitrate solution is then added. A white or yellow precipitate indicates the presence of halogen.

(2) *Nitrogen and/or Sulphur being Present.* The sodium-fusion filtrate (Part III) is made just acid to litmus by the addition of dilute nitric acid in an evaporating basin, water (5 ml.) is added, and the mixture is evaporated (*Fume Cupboard*) to half its volume. The solution is then cooled and tested for halides, as in (1) above, by the addition of nitric acid and silver nitrate solution.

DISTINCTION BETWEEN CHLORINE, BROMINE, AND IODINE

If halogen has been detected by the silver nitrate test, the sodium-fusion filtrate (Part IV) is acidified with dilute sulphuric acid, and carbon tetrachloride (2 ml.) is added. A few drops of chlorine water are then added, and the mixture is well shaken. The colour of the lower (carbon tetrachloride) layer indicates which halogen is present:

Violet	lower layer indicates iodine.		
Brown	,,	,,	,, bromine.
Colourless	,,	,,	,, chlorine.

PRACTISE USING KNOWN SUBSTANCES

Before using the sodium-fusion test for the detection of elements in unknown substances the student should carry out the tests on known substances. The following are convenient:

> Substance containing N and but *no* S (chloroacetamide).
> Substance containing N and S but *no* Hal (thiourea).
> Substance containing *no* N, Hal or S (benzoic acid).

It is most important that those tests where a *negative* result is expected should be carried out—*e.g.*, the test for halogen on thiourea.

TESTS FOR RADICALS

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Tests should be carried out in the manner and with the quantities used when studying the reactions of radicals—*i.e.*, as detailed in Chapter 12 (pp. 312-358).

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13, 7   SUBSTANCES CONTAINING C, H, (O)

Classes of Substances—Hydrocarbons (paraffin, olefin, aromatic), alcohols, phenols, ethers, aldehydes, ketones, carboxylic acids, esters.

CLASSIFICATION TESTS

TABLE 13, 7, A

Test solubility of substance in water

Soluble

**Alcohols, Phenols,
Ethers, Aldehydes,
Ketones,
Acids, Esters**

Insoluble

All Classes
See Table 13, 7, B

Test solution with litmus

Neutral

**Alcohols, Ethers,
Aldehydes, Ketones,
Esters**

Acidic

Phenols, Acids

Test substance with aqueous
DNPH [1] reagent

Precipitate [2]

Aldehydes, Ketones

No precipitate [2]

**Alcohols,
Ethers, Esters**
See Table 13, 7, C

Test substance with
Fehling's solution

Reduction

Aldehydes

No reduction

Ketones

Test substance with $NaHCO_3$

Effervescence

Acids

No effervescence

Phenols

[1] DNPH = Dinitrophenylhydrazine (see p. 331).
[2] Aldehydes or ketones give an immediate heavy precipitate. Alcohols contaminated with a trace of aldehyde or ketone give a faint precipitate on standing.

TABLE 13, 7, B

Substances insoluble in Water

Test solubility of substance in dilute NaOH

Insoluble	Soluble
All other classes	**Phenols, Acids**
	Distinguish as in
	Table 13, 7, A

Test substance with alcoholic
DNPH [1] reagent

No precipitate	Precipitate
Hydrocarbons, Alcohols,	**Aldehydes, Ketones**
Ethers, Esters	Distinguish as in
	Table 13, 7, A

Test substance with PCl₅

Test substance with PCl_5

No reaction	Reaction
Hydrocarbons, Ethers,	**Alcohols**
Esters	

Test substance with iodine

Brown solution	Red or violet solution
Ethers, Esters	**Hydrocarbons**
	See Table 13, 7, D

Try to hydrolyse substance by
refluxing with dilute NaOH

No visible change	Homogeneous solu-
	tion formed
Ether	**Ester**

[1] DNPH=Dinitrophenylhydrazine.

TABLE 13, 7, C

Alcohols, Ethers or Esters

Test substance with PCl₅

No reaction — Ethers, Esters

Reaction — Alcohols

Try to hydrolyse by refluxing
for 20 minutes with dilute
NaOH.   Acidify product
with dilute H_2SO_4 [1]

Carboxylic acid formed — **Ester**

No carboxylic acid formed — **Ether**
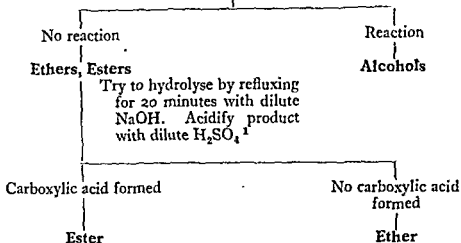
TABLE 13, 7, D

Hydrocarbons

Test substance with bromine in carbon tetrachloride

Bromine not decolorised — Paraffin, Aromatic Hydrocarbon

Bromine decolorised — **Olefin**

Test substance with fuming H_2SO_4
boil.

Substance does not dissolve — **Paraffin**

Substance dissolves — **Aromatic Hydrocarbon**
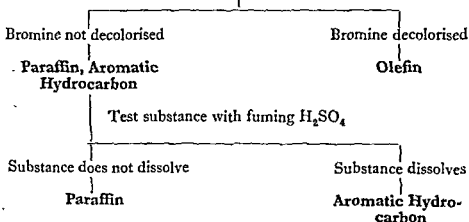
[1] Details are as follows :

Reflux the unknown substance (2 ml.) and dilute NaOH (25 ml.) for 20 minutes. Cool, acidif...
boil.
substa
smells of the original substance, the latter is an *ether*.

FURTHER TESTS

Hydrocarbons, paraffin	Permanganate.
Hydrocarbons, olefin	Permanganate.
Hydrocarbons, aromatic	Nitration.[1]
Alcohols	Esterification, sodium, oxidation with dichromate.
Phenols	Millon, ferric chloride, coupling with diazotised aniline.
Ethers	None.
Aldehydes	Ammoniacal silver nitrate, Schiff, resin formation with sodium hydroxide (given by aliphatic aldehydes only), bisulphite.
Ketones	As for aldehydes.
Carboxylic acids	Esterification, phosphorus pentachloride, ferric chloride.[2]
Esters	Examine hydrolysate for carboxylic acid and alcohol or phenol.

13, 8   SUBSTANCES CONTAINING C, H, N, (O)

Classes of Substances—Amines (primary, secondary and tertiary; aliphatic and aromatic), amides, ammonium salts of carboxylic acids, nitro compounds (aromatic).

---

[1] This must *not* be tried without a demonstrator's permission.
[2] This test must be carried out on a solution of the ammonium salt.

CLASSIFICATION TESTS

TABLE 13, 8, A

Test solubility of substance in water

Soluble	Insoluble
Amines, Amides, Ammonium Salts	**Amines, Amides, Nitro compounds** See Table 13, 8, B

Test solution with litmus

Neutral [1]	Alkaline
Amides, Ammonium Salts	**Amines**

Test substance with dilute NaOH (*cold*)

Ammonia evolved	No ammonia evolved
Ammonium Salts	**Amides**
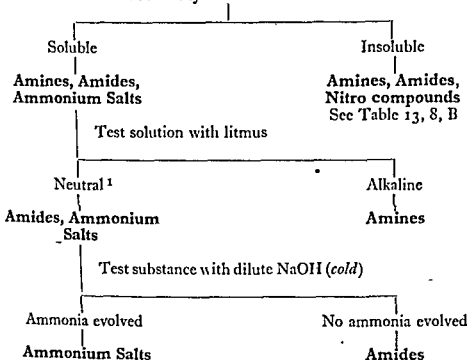
TABLE 13, 8, B

Substances insoluble in Water

Test solubility of substance in dilute HCl

Insoluble	Soluble
Amides Nitro compounds	**Amines**

Test substance with dilute NaOH (*boiling*)

Ammonia evolved	No ammonia evolved
Amides	**Nitro compounds**
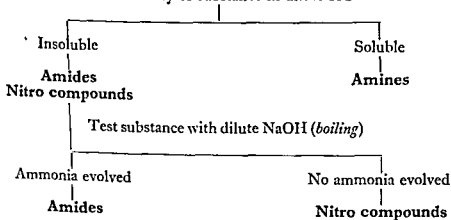
[1] Or faintly acid.

FURTHER TESTS

Amines	Classify as primary, secondary or tertiary, *and* aliphatic or aromatic (if possible) by use of nitrous acid ; acylation (if possible).
Amides . . .	*Evolution of NH₃ on boiling* [1] *with NaOH ; hydrolysis with acid.*
Ammonium Salts of Carboxylic Acids.	Liberate acid by addition of HCl and examine as far as possible.
Nitro compounds . .	Reduction to amine.

Amines	Classify as primary, secondary or tertiary, *and* aliphatic or aromatic (if possible) by use of nitrous acid ; acylation (if possible).
Amides . . .	*Evolution of NH_3 on boiling* [1] *with NaOH ; hydrolysis with acid.*
Ammonium Salts of Carboxylic Acids.	Liberate acid by addition of HCl and examine as far as possible.
Nitro compounds . .	Reduction to amine.

13, 9   SUBSTANCES CONTAINING C, H, Hal

Classes of Substances—Alkyl halides, aryl halides.

TESTS

Examine behaviour of substance with water, litmus and silver nitrate solution. Distinguish alkyl and aryl halides by boiling with dilute NaOH.

13, 10   SUBSTANCES CONTAINING C, H, N, Hal

Classes of Substances—Hydrochlorides, hydrobromides, hydriodides of all classes of amines.

TESTS

Examine behaviour of substance with water, litmus and dilute NaOH. Show that aqueous solution gives reactions of halide anion. Liberate amine and examine this as far as possible.

13, 11   SUBSTANCES CONTAINING C, H, (O), S

Class of Substances—Sulphonic acids (aromatic).

TESTS

Examine behaviour of substance with water, litmus, sodium bicarbonate solution, phosphorus pentachloride, and sodium hydroxide (fusion).

[1] If not already done.

13, 12   SUBSTANCES CONTAINING C, H, (O), N, S

Classes of Substances—Sulphonamides (aromatic), ammonium salts of sulphonic acids (aromatic), amine sulphates.

CLASSIFICATION TESTS

Test solubility of substance in water

Soluble

**Ammonium Salts of
Sulphonic Acids,
Amine Sulphates**

Insoluble

Sulphonamides

Test boiling solution with Ba(NO₃)₂ solution

Precipitate

Amine Sulphates

No precipitate

**Ammonium Salts of
Sulphonic Acids**
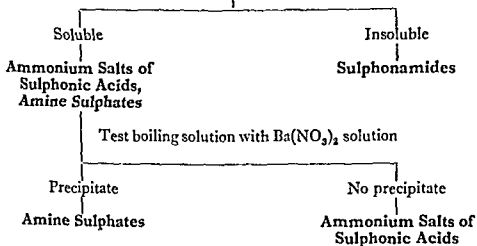
FURTHER TESTS

Sulphonamides	.	.	Solubility in cold NaOH.
Ammonium Salts of Sulphonic Acids.			Liberation of NH₃ with cold NaOH.
Amine Sulphates	.	.	Show original solution gives other reactions of sulphate anion; liberate amine and examine this.

13, 13   SUBSTANCES CONTAINING C, H, (O), METAL

Class of Substances—Metallic salts of carboxylic acids.

TESTS

Examine behaviour of substance with water, litmus and dilute HCl. Show that solution gives usual reactions of cation. Liberate acid and examine this as far as possible.

13, 14   SUBSTANCES CONTAINING C, H, (O), S, METAL

Class of Substances—Metallic salts of sulphonic acids (aromatic).

TESTS

Examine behaviour of substance with water and litmus. Show that solution gives the usual cation reactions. Fuse substance with NaOH.

FURTHER READING

See the list of books on pp. 307-308.

COMPOUNDS OF BIOLOGICAL IMPORTANCE

14, 1 ## INTRODUCTION

This chapter deals with the pure chemistry of fats, carbohydrates, proteins and some miscellaneous compounds of biological importance.[1] Many compounds of great biological importance (*e.g.*, choline, adrenaline, histamine, glucuronides) are excluded for lack of space, or because the materials are too expensive for elementary classes. The following information regarding each compound or group of compounds is presented :

Notes on general chemical and physical properties, biological function (very brief statement), and uses in medicine (if any).

Reactions. (i) Reactions which are general reactions of the substituent radicals present ; (ii) Special reactions.

Applications of the reactions in clinical work (if any) are mentioned.

The miscellaneous compounds are treated in the order in which they are likely to be met in lecture courses.

In studying each group of compounds, reference should be made to the relevant sections of Chapter 12 (pp. 309-358), which deals with the " grammar " of organic chemistry. Reports may be written in the form suggested on pp. 313-314.

FATS

14, 2 ## INTRODUCTION

The fats are chemically the least complex of the three great groups of foodstuffs. The simple fats [2] are triglycerides, *i.e.*, esters of glycerol ($CH_2OH.CHOH.CH_2OH$) with three molecules of monocarboxylic acids (fatty acids). Their general formula is

$$
\begin{array}{c}
\quad\quad\quad O \\
\quad\quad\quad \parallel \\
CH_2\text{-}O\text{-}C\text{---} R \\
| \\
\quad\quad\quad O \\
\quad\quad\quad \parallel \\
CH\text{-}O\text{-}C\text{---} R' \\
| \\
\quad\quad\quad O \\
\quad\quad\quad \parallel \\
CH_2\text{-}O\text{-}C\text{---} R''
\end{array}
$$
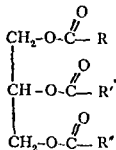
The three acyl radicals (R.CO, etc.) may be the same or different.

---

[1] The compounds include two which are of little biological importance, viz. formic acid and tartaric acid ; these are included because of their purely chemical interest.

[2] The term " fat " is used in two senses—in a wider sense as a term covering all triglycerides.

13, 14 SUBSTANCES CONTAINING C, H, (O), S, METAL

Class of Substances—Metallic salts of sulphonic acids (aromatic).

TESTS

Examine behaviour of substance with water and litmus. Show that solution gives the usual cation reactions. Fuse substance with NaOH.

FURTHER READING

See the list of books on pp. 307-308.

are, however, readily soluble in chloroform, ether or benzene (lipoid solvents).

Test the solubility of beef fat, mutton fat or lard (1 spatula-point) and olive oil (5 drops) in each of the following solvents (2 ml.)—water, ethyl alcohol, ether, chloroform.

Solids of character similar to the oils—*i.e.*, solids whose molecules contain no water-attractive radicals or only a small proportion of these —are soluble in oils. An example is the brown dye Sudan III, used in histology for staining fats. This is an azo-dye of high molecular weight containing only one water-attractive radical. It is therefore virtually insoluble in water, but readily soluble in oils.

To water (2 ml.) add Sudan III ($\frac{1}{10}$ spatula-point). The dye does not dissolve. Add olive oil (2 drops) and shake. The dye dissolves completely in the oil.

The emulsification of fats in aqueous solutions is considered on pp. 122 and 170.

MATERIALS FOR EXPERIMENTS

Natural Fats : (solid), beef fat, mutton fat, lard ;
(liquids, " oils "), olive oil, linseed oil.

Synthetic Triglycerides : tristearin, triolein.

Glycerol.

14, 3   FATS AS ESTERS. HYDROLYSIS

The most important reaction of fats is their hydrolysis (saponification) by boiling aqueous or alcoholic solutions of caustic alkalis to glycerol and the alkali salts of the fatty acids (soaps). (Compare hydrolysis of a simple ester, see p. 342.)

$$
\begin{array}{ccc}
\text{H}_2\text{C.OOC.R} & \text{H}_2\text{COH} & \text{-OOC.R} \\
| & | & \\
\text{HC.OOC.R'} \ + \ 3\text{OH}^- = & \text{HCOH} \ + & \text{-OOC.R'} \\
| & | & \\
\text{H}_2\text{C.OOC.R''} & \text{H}_2\text{COH} & \text{-OOC.R''}
\end{array}
$$
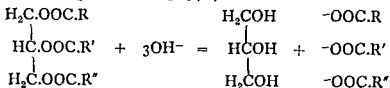
The alkali salts of the fatty acids can then be salted out by the addition of high concentrations of inorganic salts containing a common ion, or transformed into the free fatty acids by the addition of a strong acid or transformed into insoluble soaps (see reactions of carboxylic acids, p. 339).

The differences in detail between the hydrolysis of ethyl benzoate (p. 342) and the hydrolysis of a fat described below are that in the latter case (1) *alcoholic* alkali is used instead of *aqueous* alkali, (2) the acids when liberated from their salts are extracted with chloroform since they are usually too sticky to filter, (3) the alcohol glycerol, unlike ethyl alcohol, cannot be distilled out of the aqueous solution.

Fats are present in the animal body and in certain plant tissues as a food-reserve. Natural fats are usually mixtures of closely related triglycerides in which one particular substance may greatly preponderate (*e.g.*, olive oil consists very largely of triolein (glyceryl trioleate)). Natural fats usually contain a little free fatty acid (see "acid value," below) and an "unsaponifiable fraction" consisting of sterols (see pp. 434-435), other higher alcohols and hydrocarbons.

The three principal acids present as glycerides in fats are:

Palmitic acid	$CH_3.(CH_2)_{14}.COOH$	saturated.
Stearic acid	$CH_3.(CH_2)_{16}.COOH$	saturated.
Oleic acid	$CH_3(CH_2)_7.CH:CH.(CH_2)_7.COOH$	unsaturated.

Acids with shorter or longer chains, and acids with more than one double bond, are also present as glycerides.

The metallic salts of the long-chain fatty acids are called "soaps." The sodium or potassium salts, the soaps of everyday use, form colloidal solutions in water which act as detergents. Many other soaps, *e.g.*, calcium and lead soaps, are insoluble in water. Except for the specific reactions of glycerol, all the reactions described below are typical of the radicals present in the fats and their hydrolysis products. The more complex fats (phospholipins, etc.) are not considered here.

Since natural fats are mixtures of closely related substances, which cannot be separated from one another except with great difficulty, these fats are characterised by certain values which indicate the *average* chemical properties of the mixture. Among the most important values are the *saponification value* (which depends on the mean molecular weight of the fatty acids present as glycerides, and on the size of the "unsaponifiable fraction") the *iodine value* (which measures the mean degree of unsaturation) and the *acid value* (which measures the amount of free fatty acid present in the fat). The saponification and iodine values are considered in connection with the appropriate reactions be'   ''''   ' ' ' ' '' '   '
is the weigh
ise the fatty
'titration of

Fats containing a high percentage of saturated long-chain fatty acid radicals are solids at room temperature (*e.g.*, mutton fat). Fats containing a high percentage of unsaturated fatty acid radicals are liquids at room temperature and are called oils (*e.g.*, olive oil). Melting-points of some pure triglycerides are as follows:

glyceryl tristearate	(tristearin)	71°
glyceryl tripalmitate	(tripalmitin)	66°
glyceryl trioleate	(triolein)	-5°

' ''   ''' '' '   ' ' ' ' '' --- usually coloured,
ll fats are approx-
molecular weight,
solutions. They

1. Measure each fat solution (2·0 ml.) into a separate test-tube. Add to each from a burette the given solution of bromine (0·5% in carbon tetrachloride) until a permanent brown colour to match the given standard is produced. Compare the results obtained with the two fats.

REACTION WITH OSMIUM TETROXIDE

Fats containing unsaturated fatty-acid components are oxidised at the double bonds by osmium tetroxide (" osmic acid," OsO_4), the latter

2. In each of two ignition-tubes place osmium tetroxide (2% aqueous solution, 1 drop). Cover the tubes with small filter-papers and place on the papers, respectively, triolein and tristearin (5% solution in carbon tetrachloride, 1 drop). Leave to stand for an hour. The paper containing triolein is blackened by reduction-products of osmium tetroxide, that containing tristearin is not.

14, 5   GLYCEROL

Glycerol ($CH_2OH.CHOH.CH_2OH$) is a viscous sweet liquid— b.p. 290° (with decomposition) or 170°/12 mm. (without decomposition); $d = 1·26$. It is miscible in all proportions with water and is immiscible with lipoid solvents.

It has the properties expected of a trihydric alcohol (esterification gives glycerides, reaction 1) and certain special properties which serve for its identification (formation of acrolein, reaction 2).

1. Esterification.

Heat in a lightly-corked test-tube in the boiling water bath for one hour glycerol (10 drops), acetic anhydride (2 ml.), zinc chloride (anhydrous, ¼ spatula-point). Cool, make alkaline by adding concentrated aqueous sodium hydroxide cautiously with cooling under the tap. Glyceryl triacetate (triacetin) separates as an odourless oil.

2. Dehydration.

Glycerol is dehydrated on heating with potassium hydrogen sulphate ($KHSO_4$), giving the pungent-smelling unsaturated aldehyde acrolein.

$$
\begin{array}{ccc}
CH_2OH & & CH_2 \\
| & & \parallel \\
CHOH & = & CH + 2H_2O \\
| & & | \\
CH_2OH & & CHO
\end{array}
$$
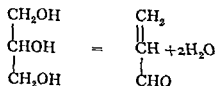
The *saponification value* of a fat is the number of milligrams of potassium hydroxide required to hydrolyse 1·000 g. of the fat. The fat is refluxed with an excess of standard alcoholic potassium hydroxide and the excess determined by back titration with standard acid.

Hydrolysis of a Fat

Mix the fat or oil (0·5 g.) with alcoholic sodium hydroxide solution (10%, 10 ml.) in a conical flask, and reflux the mixture on the boiling water bath until an almost clear solution is obtained. (About thirty minutes' heating will be required.) Then pour the mixture into water (100 ml.). The resulting solution (which should be free from oily drops) contains sodium soaps and glycerol. Set aside 15 ml. of this solution for use in experiments on the soaps (see below).

Pour the remainder of the aqueous solution into a separating-funnel, acidify it with dilute sulphuric acid and extract the water-insoluble material with chloroform (two successive 5 ml. portions). Wash the combined chloroform extracts with water (two successive 5 ml. portions), and then evaporate the chloroform in a distillation apparatus on the water bath. Dissolve the residue, which consists of the fatty acids, in warm ethyl alcohol (3 ml.), and test the resulting solution with damp litmus-paper.

During the extractions with chloroform the glycerol remains in the aqueous solution.

Use the aqueous soap solution (15 ml.) previously set aside for the following experiments (see reactions 2 (*b*) and (*c*) of carboxylic acids, p. 339).

Salting out of sodium soap.
Precipitation of calcium soap.
Precipitation of magnesium soap.

14, 4   UNSATURATION IN FATS

REACTION WITH HALOGENS

The olefinic double bonds in unsaturated fats and fatty acids combine with bromine (or iodine) as do those in simple olefins (compare p. 316). The reaction between oleic acid and bromine is

$$CH_3(CH_2)_7.CH:CH.(CH_2)_7.COOH + Br_2$$
$$= CH_3(CH_2)_7.CHBr.CHBr.(CH_2)_7.COOH.$$
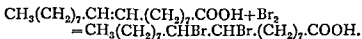
This reaction is used to detect and to determine unsaturation in fats and fatty acids.

The *iodine value* of a fat is the number of grams of iodine absorbed by 100 g. of the fat. For details of determination see other books.

The solutions provided for a rough comparison of a saturated and unsaturated fat are 1% solutions in carbon tetrachloride of mutton fat (mainly saturated triglycerides) and of linseed oil (containing glycerides of the highly unsaturated linoleic and linolenic acids).

2. "*Reserve.*"—Polysaccharides stored in the animal or plant, and hydrolysed to monosaccharides as required for the production of energy (*e.g.*, glycogen, starch).[1]

3. "*Structural.*"—Polysaccharides used as the framework of cells, chiefly in plants (*e.g.*, cellulose).

Many different carbohydrates are used in bacteriological work as culture media for different organisms.

The many important reactions of carbohydrates—hydrolysis of polysaccharides and disaccharides, various decompositions of monosaccharides, including fermentations yielding ethyl alcohol and lactic acid and carbon dioxide—which take place under the influence of enzymes are not dealt with in this book.

MONOSACCHARIDES

These were, at one time, thought to be true polyhydroxy-aldehydes (aldoses) or polyhydroxy-ketones (ketoses), *e.g.*,

$CH_2OH.(CHOH)_4.CHO$, an aldohexose (*e.g.*, glucose).
$CH_2OH.(CHOH)_3.CO.CH_2OH$, a ketohexose (*e.g.*, fructose).
$CH_2OH.(CHOH)_3.CHO$, an aldopentose (*e.g.*, xylose).

It is now known that the pentoses and hexoses exist chiefly as internal ethers (semi-acetals) which may be called *modified* poly-hydroxy-aldehydes or ketones.
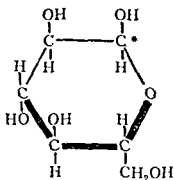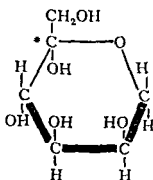
α-*d*-glucopyranose [2] β-*d*-fructopyranose [2]

* The carbon atoms marked thus are the carbon atoms of potential aldehyde or ketone radicals.

The pentoses and hexoses exist in aqueous solution as tautomeric mixtures ; *e.g.*, *d*-glucose exists mainly as the two pyranose forms, α

[1] Disaccharides serve both as " mobile " and " reserve " carbohydrates.
[2] The term " pyranose " refers to the six-membered pyran ring in these structures.

A similar reaction takes place with concentrated sulphuric acid. Fats also yield acrolein when heated with potassium hydrogen sulphate or concentrated sulphuric acid.

    (*a*) To potassium hydrogen sulphate (half an inch in a *dry* test-tube) add glycerol (5 drops), stir, and heat until charring just begins. Acrolein is formed (smell cautiously).

    (*b*) To concentrated sulphuric acid (1 ml.) add glycerol (5 drops). The mixture chars; acrolein and sulphur dioxide are evolved (smell).

CARBOHYDRATES

14, 6   INTRODUCTION

The simple carbohydrates, the monosaccharides, are modified[1] polyhydroxyaldehydes or polyhydroxyketones of the general formula $C_nH_{2n}O_n$. The most important monosaccharides are the trioses, pentoses and hexoses (n=3, 5, 6 respectively). The molecules of the more complex carbohydrates, disaccharides and polysaccharides, consist of two or more monosaccharide (usually hexose) units joined by ether linkages of a special type called glycosidic linkages.

Most of the reactions of carbohydrates described below are those expected of . . . . ls, modified[1] carbc . . .

All . . . . and neutral. Monosaccharides and disaccharides are readily soluble in water and insoluble in lipoid solvents, on account of the large proportion of hydroxyl radicals in their molecules. These substances taste sweet and are called sugars. Polysaccharides either form hydrophilic colloidal solutions in water or do not dissolve in water at all, depending on their molecular weights. All polysaccharides are insoluble in lipoid solvents. Those which form colloidal solutions in water form gels in certain circumstances, and are precipitated from their solutions by high concentrations of electrolytes or by alcohol (see pp. 124-126).

One of the most important physical properties of a carbohydrate is its optical rotation. (Determination of this is suitable for a demonstration, but not for a class experiment.)

From the biological point of view carbohydrates may be classed as follows:

1. "*Mobile*."—Monosaccharides, whose breakdown in the tissues provides energy (*e.g.*, glucose).[3]

---

[1] The meaning of the word "modified" is explained in the paragraphs dealing with monosaccharides, p. 381.

[2] Many impure samples are yellow or brownish.

[3] Disaccharides serve both as "mobile" and "reserve" carbohydrates.

with alkali in the presence of certain oxidising agents, the latter are reduced by some products of the alkaline decomposition of the sugar. The reduction of such oxidising agents (chiefly complex cupric ions) serves for the detection and estimation of the sugars (see pp. 387-390).

Two hexoses (glucose and fructose) and one pentose (xylose) are studied here. Glucose and fructose occur in nature free in many fruit juices and combined in di- and poly-saccharides (see these). Xylose occurs combined in some plant polysaccharides.[1] Glucose and fructose are identical in so far as the configuration at carbon atoms 3, 4 and 5 is concerned ; certain derivatives (e.g., the osazone) are therefore identical (see pp. 384-386). Other hexoses, e.g., galactose, differ from glucose and fructose in the configuration at carbon atoms 3, 4 or 5.

DISACCHARIDES

The molecules of these consist of two monosaccharide units joined by a glycosidic linkage. The three common disaccharides studied here are composed of two hexose units each (molecular formulæ $C_{12}H_{22}O_{11}$). They are as follows:

Maltose=glucose+glucose—water (source, partial hydrolysis of starch).

Lactose=glucose+galactose—water (source, milk).

Sucrose=glucose+fructose—water (source, cane sugar or beet).

All disaccharides are hydrolysed to their constituent monosaccharides by boiling with dilute mineral acids (see p. 393).

In maltose and lactose, the potential aldehyde radical of one unit is linked to an ordinary hydroxyl radical of the other unit, while the potential aldehyde radical of the second unit is free. The molecule therefore forms carbonyl derivatives (e.g., osazones); like the monosaccharides it undergoes with alkali complex changes, the products of which have reducing properties (see p. 388). Maltose and lactose are therefore called "reducing disaccharides."

In sucrose the potential aldehyde radical of the glucose unit is linked to the potential ketone radical of the fructose unit ; the molecule therefore forms no carbonyl derivatives, is not changed by alkali and has no reducing properties. Sucrose is therefore called a "non-reducing disaccharide."

POLYSACCHARIDES

The molecules of these are built up of many monosaccharide units, each linked to the next by a glycosidic linkage (see pp. 82-84). Some polysaccharide .... neral acids, though the structural .... pp. 393-395).

All the pol. .... hexose units and have the general formula $(C_6H_{10}O_5)_n$; they are as follows:

---

[1] It is used here as an example because it is cheap. Other pentoses, e.g., ribose, which are of great importance in animal physiology are too expensive for use here.

(shown above and III below) and β (IV), together with small proportions of the free aldehyde (I) and probably other forms, including the intermediate aldehydrol (II).

	aldehyde I	aldehydrol II	α-glucopyranose III	β-glucopyranose IV
		HO OH		
1	CHO	CH	H.C.OH	HO.C.H
2	H.C.OH	H.C.OH	H.C.OH	H.C.OH
3	HO.C.H	HO.C.H	HO.C.H	HO.C.H
4	H.C.OH	H.C.OH	H.C.OH O and	H.C.OH
5	H.C.OH	H.C.OH	H.C	H.C
6	CH₂OH	CH₂OH	CH₂OH	CH₂OH

with $\pm H_2O \rightleftharpoons$ between aldehyde and aldehydrol, and $\pm H_2O \rightleftharpoons$ between aldehydrol and α-glucopyranose.

Numbering of carbon atoms
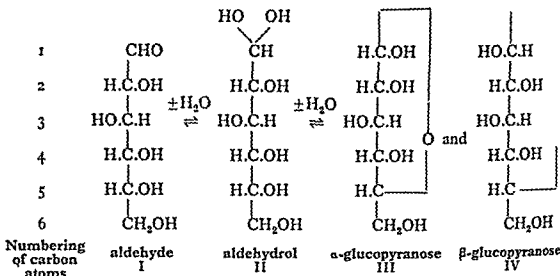
The existence of such a tautomeric mixture explains why monosaccharides act as carbonyl compounds readily with some reagents (*e.g.*, phenylhydrazine, see p. 384), but *not* with others (*e.g.*, Schiff's reagent, see p. 386). The hydroxyl radicals on the potential aldehyde or ketone carbon atoms form hydroxyl derivatives, *e.g.*, ethers of a special kind called glycosides. (The formation of these cannot be illustrated in an elementary course. Some reactions of a typical glycoside are considered on pp. 433-434.)

potential aldehyde   potential ketone
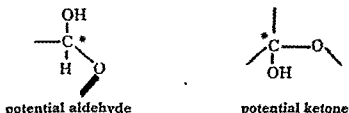
The ordinary hydroxyl radicals on the other carbon atoms form the usual derivatives (*e.g.*, esters, see p. 387).

Monosaccharides (both aldoses and ketoses) undergo very complex changes and decompositions under the influence of alkali, which probably begin with the enolisation of the carbonyl group.

$$-CO-CH- \quad \rightleftharpoons \quad -C(OH)=C-$$

If monosaccharides are heated with alkali alone, brown resins smelling of caramel are produced (see pp. 387-388). If monosaccharides are heated

14, 8 CARBOHYDRATES AS HYDROXY COMPOUNDS

ACETYLATION

The hydroxyl radicals of carbohydrates may be acetylated in the usual way with acetic anhydride in the presence of sodium acetate or zinc chloride. Thus glucose gives a penta-acetate :

$$\begin{array}{c} -\text{CHOH} \\ \text{O (CHOH)}_3 \\ -\text{CH} \\ \text{CH}_2\text{OH} \end{array} + 5(\text{CH}_3\text{CO})_2\text{O} = \begin{array}{c} -\text{CHO.OC.CH}_3 \\ \text{O (CHO.OC.CH}_3)_3 \\ -\text{CH} \\ \text{CH}_2\text{OC.CH}_3 \end{array} + 5\text{CH}_3.\text{COOH}$$
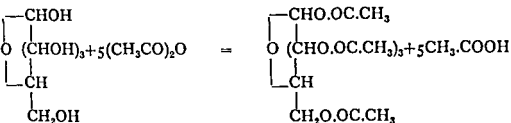
1. To solid glucose (2 spatula-points) add acetic anhydride (1 ml.) and anhydrous zinc chloride ($\frac{1}{2}$ spatula-point), and heat in the boiling water bath for 30 minutes. Cool and add water (10 ml.) ; penta-acetylglucose separates as an oil, which solidifies on standing and scratching.

CHARRING

All carbohydrates, like other compounds containing a number of CHOH groups (*e.g.*, tartaric acid), char on heating alone or with concentrated sulphuric acid. The reaction is probably in part a dehydration and may be represented roughly thus :

$$\text{H}-\overset{|}{\underset{|}{\text{C}}}-\text{OH} \rightarrow -\overset{|}{\underset{|}{\text{C}}}-+\text{H}_2\text{O}.$$
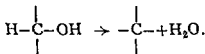
2. Heat *solid* glucose (1 spatula-point) slowly in an ignition tube. The compound melts, froths, goes brown and then black, and smells of " burnt sugar."

3. Heat *solid* glucose (1 spatula-point) and concentrated sulphuric acid (1 ml.) slowly in a test-tube. The mixture goes yellow, then brown and finally black, and smells of " burnt sugar " and sulphur dioxide.

14, 9 BEHAVIOUR WITH ALKALI AND OXIDISING AGENTS

Reducing sugars (*i.e.*, sugars containing a free potential aldehyde or ketone radical) undergo under the influence of alkali very complex changes and decompositions, which probably begin with the enolisation of the carbonyl radical.

$$-\text{CO}-\overset{|}{\underset{|}{\text{CH}}}- \rightleftharpoons -\text{C(OH)}=\overset{|}{\underset{|}{\text{C}}}-$$
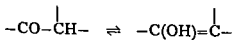
Non-reducing sugars (*e.g.*, sucrose) do not undergo these changes.

In the second stage, the primary alcohol radical on the first carbon atom is oxidised to an aldehyde radical.

$$\begin{array}{ccc} CH_2OH & +H_2N.NH.C_6H_5 & HC{:}O & +C_6H_5NH_2+NH_3 \\ | & & | & \text{Aniline} \\ C{:}N.NH.C_6H_5 & = & C{:}N.NH.C_6H_5 \\ | & & | \\ & & \text{Fructosone} \\ & & \text{phenylhydrazone} \end{array}$$
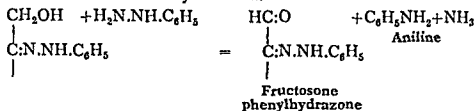
In the last stage phenylhydrazine reacts with the newly formed carbonyl radical, giving the osazone.

$$\begin{array}{ccc} HC{:}O & +H_2N.NH.C_6H_5 & HC{:}N.NH.C_6H_5+H_2O \\ | & & | \\ C{:}N.NH.C_6H_5 & = & C{:}N.NH.C_6H_5 \\ | & & | \\ & & \text{Phenylfructosazone} \\ & & \text{(=Phenylglucosazone)} \end{array}$$
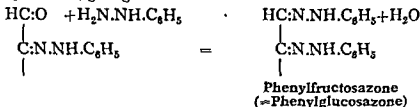
The condensations are carried out with an aqueous solution of phenylhydrazine acetate at 100°. Prepare the osazones of glucose, fructose, maltose and lactose simultaneously as follows :

1. To each carbohydrate solution (10 ml.) in a test-tube add an aqueous solution of phenylhydrazine acetate (1 ml.).[1] Stopper the tubes with corks from which air-gaps have been cut and which are marked with the names of the carbohydrates used. Heat the tubes in a boiling water bath. After 30 minutes' heating remove the glucose and fructose tubes, in which yellow precipitates will have formed, and allow them to cool slowly in your test-tube rack. After 60 minutes' heating turn out the burner under the water bath and allow the latter to *cool slowly with the maltose and lactose tubes in it.* When the bath is cold (not before) remove the maltose and lactose tubes. These should now contain crystalline precipitates.

Examine the precipitates in the four tubes under a low-power microscope. This can conveniently be done while the precipitates are still in the tubes by tilting the microscope so that the stage is at an angle of about 45° to the horizontal. Note that the crystals of the osazones clump themselves together in characteristic ways ; only in the case of maltosazone is the shape of the individual crystals obvious. See Fig. 14, 1. Draw your own crystals in your notebook.

Schiff's Reaction

The " potential aldehyde " radicals of aldoses do *not* give pink colours with Schiff's reagent (contrast true aldehydes, p. 334).

2. To Schiff's reagent (2 ml.) add glucose solution (2 ml.) and shake. The mixture remains colourless.

[1] The solution contains phenylhydrazine (200 g. per litre) and acetic acid (200 g. per litre).

sugar in urine, and is less readily reduced than Fehling's solution by some substances which are normal constituents of urine (*e.g.*, uric acid).

Benedict's Reagent (quantitative, 1911).

The contents are as for the qualitative reagent *plus* potassium thiocyanate and potassium ferrocyanide. The reduction product is white cuprous thiocyanate instead of red cuprous oxide ; the end-point is therefore easier to distinguish. The ferrocyanide prevents atmospheric oxidation of cuprous compounds.

Folin-McElroy Reagent (qualitative, 1918).

This contains sodium carbonate and sodium phosphate. Copper is present as a complex cupric phosphate ion. The solution keeps indefinitely. The reduction product is cuprous oxide. The advantage of this reagent over Benedict's is that phosphate is cheaper than citrate.

Folin-McElroy Reagent (quantitative, 1918-19).

The contents are as for the qualitative reagent *plus* potassium thiocyanate. The reduction product is white cuprous thiocyanate.

Qualitative Reductions.

Carry out each of the following tests with glucose (monosaccharide, reducing), lactose (disaccharide, reducing), sucrose (disaccharide, non-reducing) :

2. *Fehling's Test.*

Mix Fehling's Solutions No. 1 and No. 2 (1 ml. of each), add the carbohydrate solution (2 ml.) and boil. The cupric salt is *rapidly* reduced to red or yellow cuprous oxide by glucose or lactose, but *not* by sucrose.

3. *Fehling's Test (Alternative Method).*

Mix in one test-tube Fehling's Solutions No. 1 and No. 2 (1 ml. of each) and take in a second test-tube the carbohydrate solution (2 ml.). Heat the two solutions to boiling simultaneously. Pour the carbohydrate solution into the Fehling's Solution. *Immediate* reduction to yellow or red cuprous oxide takes place with glucose and lactose, but not with sucrose.

4. *Benedict's Test.*

To Benedict's qualitative reagent (5 ml.) add the carbohydrate solution (8 drops), heat for 2 minutes in a boiling water bath and allow to cool in your test-tube rack. Results are as in 2.

5. *Folin-McElroy Test.*

Repeat 4, using Folin-McElroy qualitative reagent (5 ml.) instead of Benedict's reagent. Results are as in 2 and 4.

If the sugars are heated with alkali *alone*, brown resins smelling of caramel are produced.

    1. To bench sodium hydroxide solution (3 ml.) add *solid* glucose (1 spatula-point) and boil. The solution becomes yellow and smells of caramel.

If reducing sugars are heated with alkali in the presence of certain *oxidising agents*, the latter are reduced by some products of the alkaline decomposition of the sugar. These reductions are used for the detection and the volumetric determination of the sugars.

The substances reduced by sugars in the common tests and their reduction products are

(1) Cupric compounds, reduced to cuprous compounds.
(2) Silver compounds, reduced to silver metal.
(3) Ferricyanides, reduced to ferrocyanides.

In all these reactions it is essential to adhere strictly to the conditions found suitable by previous workers, especially when the reactions are being used for approximate or exact quantitative determinations; otherwise misleading results will be obtained.

The quantitative reagents do not react according to any definite stoichiometric equation. An empirical factor must be used for each reagent and each carbohydrate, e.g., 10·0 ml. Benedict's quantitative reagent are reduced by 20·0 mg. glucose.

ALKALINE CUPRIC SALT REAGENTS

A number of different alkaline cupric salt reagents have been devised. It is interesting to note how the original reagent (Fehling's) has been modified for the sake of greater convenience and smaller cost. All these reagents contain cupric sulphate, an alkali, something to keep cupric ions in solution in presence of alkali, and in some cases, further reagents. Details are as follows :

Fehling's Reagent (qualitative or quantitative, 1849).

    This contains sodium hydroxide and sodium potassium tartrate. Copper is present as a complex cupric tartrate ion. The solution will not keep and must be made fresh as required. The reduction product is red cuprous oxide. The reagent is used clinically in testing urine qualitatively for sugar. Care must be taken to ensure that slow reduction of cupric salt by normal constituents of urine (e.g., uric acid) is not confused with rapid reduction by abnormal quantities of sugar.[1]

Benedict's Reagent (qualitative, 1909).

    This contains sodium carbonate and sodium citrate. Copper is present as a complex cupric citrate ion. The solution keeps indefinitely. The reagent is used for a quick roughly-quantitative estimation of

---

[1] The behaviour of uric acid with this reagent will be studied later (p. 428).

14, 10   OTHER OXIDATIONS

The oxidation of sugars by *cupric salts in acidic solution is important.*
The reagent used (Barfoed's) contains cupric acetate and acetic acid.
It is reduced by all monosaccharides, but not by disaccharides (not even
those which reduce the alkaline copper reagents).

Test glucose, fructose, and lactose as follows :

Boil Barfoed's reagent (2 ml.) and add 10 drops of the carbo-
hydrate solution slowly from a dropping pipette, boiling con-
tinuously. Reduction (formation of a faint red scum of cuprous
oxide on the surface of the liquid) occurs with glucose and fructose,
but *not* with lactose.

The oxidations of monosaccharides by bromine water and by nitric
acid to give carboxylic acids are not considered here.

14, 11   FURFURAL-PHENOL REACTIONS

Carbohydrates are converted by concentrated mineral acids into
derivatives of furfural,
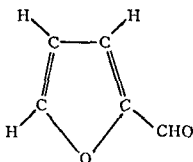
which then condense with phenols to give highly coloured products.

The following modifications of this test are of importance :

Test	Mineral Acid	Phenol	*Coloured Products formed by :*
Molisch's .	Conc. H_2SO_4	α-Naphthol	All carbohydrates
Selivanoff's .	Conc. HCl	Resorcinol	Ketohexoses and sucrose [1]
Bial's .	Conc. HCl	Orcinol [2]	Pentoses
Tollens' .	Conc. HCl	Naphtho-resorcinol [3]	Glucuronic acid Glucuronic acid

[1] Because sucrose is hydrolysed, giving fructose, in the conditions of the test.
[2] 5-Methylresorcinol.   [3] 1 : 3-Dihydroxynaphthalene.

Quantitative Determination of Reducing Sugar by Benedict's Method

The reaction does not follow any known equation, and the calculation is based on an empirical relationship. In the conditions detailed here 10·0 ml. reagent are reduced by 20·0 mg. glucose, 21·2 mg. fructose, 27·1 mg. lactose, or 29·6 mg. maltose. The reaction is carried out at the boiling-point of the reagent. If a burette fitted with a glass tap is used, the tap lubricant is heated and softened by the steam from the reaction mixture, and the tap tends to leak. A burette fitted with a spring clip on a piece of rubber tubing is preferable (see Fig. 14, 2).

ate (2–3 g.) and a few porous chips. Clamp the boiling-tube and a burette containing the sugar solution in the positions shown in Fig. 14, 2. Bring the Benedict's solution to the boil with a *small* Bunsen flame and run in the sugar solution until the end-point (pale blue to *white*) is reached, boiling the mixture continuously. Towards the end of the titration add the sugar solution dropwise, allowing thirty seconds' boiling between successive drops. Add water if necessary to replace that lost by evaporation.

Fig. 14, 2
Apparatus for Benedict Titration

ALKALINE SILVER SALT REAGENTS

Silver salts in alkaline solution (*e.g.*, ammoniacal *silver nitrate*) are reduced to metallic silver by all reducing sugars. The test, which is little used now, is carried out as for aldehydes (see p. 333).

FERRICYANIDE REAGENT

The reduction of ferricyanides to ferrocyanides by reducing sugars forms the basis of the widely used Hagedorn-Jensen method for determining blood sugar.

7. Mix potassium ferricyanide (1% aqueous solution, 2 ml.) bench sodium hydroxide (1 ml.) and glucose solution (1 ml.) and boil for 2 minutes. The yellow ferricyanide is reduced to colourless ferrocyanide.

14, 13 IODINE REACTIONS

The colloidal solutions of some polysaccharides in water give distinctive colours with iodine as follows:

Polysaccharide	Colour with Iodine
Starch . . .	Blue
Dextrins . .	Purple, red or brown
Glycogen . .	Brownish-red

The blue starch-iodine colour is due to an adsorption-complex ; presumably the other colours are due to similar complexes. The colours are discharged on heating, and reappear on cooling the solutions.

The colours with dextrins will be seen in the experiment on the hydrolysis of starch (see p. 394). Carry out the following test with starch and glycogen solutions, and with water as a control:

To the carbohydrate solution or water (1 ml.) add dilute iodine in aqueous potassium iodide (1 drop). Compare the colours produced.

14, 14 HYDROLYSIS OF DI- AND POLY-SACCHARIDES

All disaccharides and many polysaccharides are hydrolysed by hot dilute mineral acid. Certain polysaccharides used by plants as cell-walls (i.e., as an inert " scaffolding ") are unaffected by boiling dilute acid or alkali but are hydrolysed by concentrated acids.

Hydrolysis of Disaccharides.

Sucrose (a non-reducing disaccharide) is rapidly hydrolysed by hot dilute mineral acid to an equimolecular mixture of glucose and fructose, which have reducing properties. Maltose and lactose are hydrolysed similarly.

$$C_6H_{11}O_5.O.C_6H_{11}O_5 + H_2O \rightleftharpoons 2C_6H_{11}O_5.OH.$$
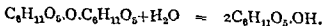
1. To sucrose solution (2 ml.) in a boiling-tube add dilute hydro-

neutralised solution and show that it reduces Fehling's solution. Use the remainder of the neutralised solution to prepare the osazone of the monosaccharides.

2 C

Details of these tests—except Tollens' test (which requires very expensive materials)—are as follows :

Molisch's Test.

1. *To the carbohydrate solution (e.g., glucose, 1 ml.) add an alcoholic solution of α-naphthol (1 drop).* Take in an ignition-tube pure (A.R. quality) [1] concentrated sulphuric acid (1 ml.) and run the solution containing carbohydrate and α-naphthol on to the surface of this from a pipette so that it forms a separate upper layer. On slight mixing of the two layers a violet ring appears at the interface.

Selivanoff's Test.

Carry out the following test with fructose, glucose and sucrose:

2. To Selivanoff's reagent (resorcinol in hydrochloric acid, 2 ml.) add the carbohydrate solution (5 drops). Boil for half a minute. A red or brown colour or precipitate is produced with fructose and sucrose. A very faint colour is produced with glucose. (Note the value of a control test here.)

Bial's Test.

Carry out the following test with xylose and glucose:

3. To the carbohydrate solution (2 ml.) add Bial's reagent (orcinol in hydrochloric acid, 2 ml.) and boil for thirty seconds. The xylose solution becomes yellow-green, and then green on standing. The glucose solution becomes yellow and remains yellow on standing.

14, 12   FOULGER'S TEST

Foulger's reagent is an aqueous solution of sulphuric acid, stannous chloride and urea. It gives a blue colour with fructose and with sucrose (which in the conditions of the test is hydrolysed, giving fructose). The reagent gives no colour with other carbohydrates. The chemistry of the reaction is unknown. Carry out the following test with fructose, glucose and sucrose:

To Foulger's reagent (2 ml.) add the carbohydrate solution (10 drops) and boil for 45 seconds, shake vigorously, and leave to stand. The colour, if any, develops slowly.

[1] *Pure* sulphuric acid *must* be used for this test. Impure sulphuric acid gives a green ring, whether or not carbohydrate is present.

sulphuric acid, by cuprammonium hydroxide solution (Schweizer's reagent) or by aqueous zinc chloride solution. All these changes are ascribed to partial hydrolysis of the cellulose. The partly hydrolysed cellulose obtained by solution in concentrated sulphuric acid can be completely hydrolysed to glucose by dilution of the acid solution and boiling. Cellulose can be reprecipitated from Schweizer's reagent, giving, in suitable conditions, one form of "artificial silk."

3. *Complete Hydrolysis.*

Stir a small pad of cotton wool with concentrated sulphuric acid (5 ml.) in a beaker until an almost clear solution is obtained. Pour this solution into water (50 ml.) in a flask, and boil the

4. *Partial Hydrolysis—Preparation of Parchment-Paper.*

To water (2·5 ml.) add cautiously concentrated sulphuric acid (5 ml.) and cool the solution thoroughly. Dip half of a strip of filter-paper into the cold solution for a few seconds, then wash the strip thoroughly with water and allow it to dry. Note that the acid-treated half of the paper is much tougher than the untreated half.

5. *Partial Hydrolysis—Behaviour of Cellulose with Various Reagents.*

Grind up small pieces of filter-paper with the following reagents (5 ml. each) in turn : 20% aqueous sodium hydroxide solution, Schweizer's reagent, saturated aqueous zinc chloride solution. The paper "dissolves" in each case. Add a few drops of the " solution " of filter-paper in Schweizer's reagent to an excess of dilute hydrochloric acid ; cellulose is reprecipitated.

14, 15   AGAR

Agar, which is a polysaccharide composed of galactose units, forms the cell walls of certain seaweeds. On treatment with water it does not dissolve, but swells up to form a jelly. Agar is hydrolysed only with difficulty by acids, and is not attacked by bacteria, or by digestive enzymes in the human digestive tract. These properties are useful to the bacteriologist since they enable him to grow bacteria on a solid medium ; they are also useful to the physician since they provide him with a means of treating certain kinds of constipation by increasing the bulk of indigestible residues in the diet.

Half fill an ignition-tube with water. Add a few pieces of agar, and examine after two hours. The agar will have swollen to many times its original volume.

Hydrolysis of Starch.

Starch is hydrolysed by hot dilute mineral acid, giving first poly-saccharides of smaller molecular weight called dextrins, then the disaccharide maltose, and finally glucose. The reactions may be represented very roughly as follows :

$$(C_6H_{10}O_5)_{21} \rightarrow 2(C_6H_{10}O_5)_{12} \rightarrow 4(C_6H_{10}O_5)_6$$
$$\text{starch} \qquad\qquad \text{dextrins}$$

$$\cdots\cdots \rightarrow 12C_{12}H_{22}O_{11} \rightarrow 24C_6H_{12}O_6$$
$$\text{maltose} \qquad\qquad \text{glucose}$$
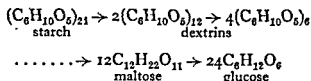
The first part of the reaction may be followed by testing the reaction mixture with iodine after various periods of heating. Glucose may be recognised at the end of the reaction by the formation of its osazone.

2. Mix starch solution (1%, 20 ml.) and dilute hydrochloric acid (5 ml.) in a measuring cylinder. Transfer 3 ml. of the mixture to each of eight test-tubes (I-VIII). To tube I immediately add water (3 ml.) and iodine in potassium iodide (2 drops) and shake. Place the remaining tubes in a boiling water bath and keep them in the bath for the times stated below. As each tube from II to VII inclusive is removed, cool it under the tap, and add water and iodine solution as for tube I. Shake and compare the colours produced, which should be *approximately* as stated below. Cool tube VIII, neutralise its contents, and use them for the preparation of glucosazone.

Tube	Time of heating (minutes)	Colour with Iodine
I	0	Blue
II	5	Purple-blue
III	10	Purple
IV	15	Brownish-purple
V	20	Brown
VI	25	Yellow
VII	30	Very pale yellow [1]
VIII	40	(Use for osazone)

Hydrolysis of Cellulose.

Cellulose is altered in nature by 20% sodium hydroxide solution or by 80% sulphuric acid, and it is " dissolved " by concentrated

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[1] Compare this colour with that of a blank test carried out by adding the iodine solution (1 drop) to water (6 ml.).

AMINO-ACIDS AND PROTEINS

14, 17   INTRODUCTION

Amino-acids are compounds containing at least one amino radical and one carboxyl radical, the simplest being glycine, $H_2N.CH_2.COOH$. Since the amino radical confers basic properties and the carboxyl radical acidic properties, amino-acids act either as bases or acids according to circumstances, *i.e.*, they are amphoteric electrolytes.

The amino-acids are white solids; those of lower molecular weight are readily soluble in water, while those of higher molecular weight are sparingly soluble in water, but " soluble " in acids and alkalis due to salt formation.

Proteins are solid compounds of high molecular weight (a few thousands to several millions) consisting chiefly of large numbers of α-amino-acid units ($-NH.CHR.CO-$) linked together by amide (peptide) linkages ($-CO.NH-$). Proteins are essential constituents of all living cells and, together with water, they form the greater part of most cells. It cannot be too strongly emphasized that proteins are by far the most complex compounds with which the chemist has to deal, and that many statements made in this and later sections are very great simplifications justified only by convenience.

Since the amino-acid units in proteins include monoaminodicarboxylic acids and diaminomonocarboxylic acids, each protein molecule contains numbers of free carboxyl radicals and free amine radicals, and is therefore amphoteric. The amphoteric nature of amino-acids and proteins is considered at the end of this section.

Some of the amino-acid units present in proteins contain substituent radicals other than amino and carboxyl. On these other radicals depend many specific reactions of these amino-acids and of the proteins containing them.

Proteins can be hydrolysed into their constituent amino-acids by hot dilute acids or alkalis, or by enzymes. The following is an example

colloidal solution (test this
insoluble: agar swells on

14, 16   CLASSIFICATION OF CARBOHYDRATES

Carbohydrates may be classified, and in some cases identified, by means of the reactions described in the preceding sections. A method is outlined below. Reports should be written in a form similar to that given in Chapter 13 (pp. 362-363) for simple organic classifications.

Note appearance of sample.
Test solubility of sample (0·1 g.) in cold water (20 ml.) added gradually.

Insoluble
Most Polysaccharides[1]

Soluble
Some Polysaccharides and all Di- and Mono-saccharides

Do Benedict's test

No reduction
All Soluble Polysaccharides and all Non-reducing Disaccharides[2]

Reduction
Reducing Disaccharides and all Monosaccharides

Do Barfoed's test

No reduction
Reducing Disaccharides[3]

Reduction
All Monosaccharides

Do Selivanoff's test

Red colour
Ketoses[3]

No red colour
Aldoses

Do Bial's test

Green colour
Aldopentoses[4]

No green colour
Aldohexoses[4]

[1,2,3,4] See opposite page.

4. *Reactions of Non-amino-acid Constituents and of Proteins containing them* (Sections 14, 21-22, pp. 410-414).

These sections deal with the reactions of haemoglobin and related compounds, of phosphates and of carbohydrates.

THE AMPHOTERIC NATURE OF AMINO-ACIDS AND PROTEINS

α-Amino-acids formerly represented by the general formula $H_2N.CHR.COOH$ are now believed to exist chiefly as *dipolar ions*, $^+H_3N.CHR.COO^-$, *i.e.*, ions which carry both a negative and a positive charge and which are therefore electrically neutral. These ions may be considered as internal salts, the hydrogen ion from the carboxyl radical having attached itself to the amino radical.

The behaviour of dipolar ions with acids and bases may be represented as follows: Suppose a strong acid is added to a solution containing the dipolar ion; the carboxyl radical being weakly acidic, added hydrogen ion combines with the $.COO^-$ group thus:

$$^+H_3N.CHR.COO^- + H^+ \;=\; ^+H_3N.CHR.COOH \qquad . \quad . \; (A)^1$$
$$\text{(dipolar ion; neutral)} \qquad\qquad \text{(cation)}$$
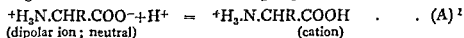
The amino-acid acts as a base and is present as a cation. Suppose, on the other hand, a strong base is added to the dipolar ion. The amino radical being weakly basic, added hydroxyl ions react with the ^+H_3N group thus:

$$^+H_3N.CHR.COO^- + OH^- \;=\; H_2N.CHR.COO^- + HOH \qquad . \; (B)^1$$
$$\text{(dipolar ion; neutral)} \qquad\qquad \text{(anion)}$$
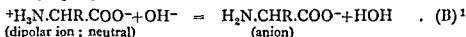
The amino-acid acts as an acid and is present as an anion.

The *p*H value of the solution in which the amphoteric electrolyte is electrically neutral, and is present as dipolar ions or uncharged molecules, is called its *iso-electric* point (*p*I). The iso-electric points of some typical amino-acids are as follows:

glycine, 6·0 ; tyrosine, 5·7 ; cystine 5·0.

If the *p*H value of a solution is below (*i.e.*, on the acid side of) the iso-electric point, reaction (A) takes place, the amino-acid acting as a base ; if the *p*H value is above (*i.e.*, on the alkaline side of) the iso-electric point, reaction (B) takes place, the amino-acid acting as an acid.

Each protein molecule contains many free carboxyl and many amino radicals (in side-chains) and the behaviour of proteins with acids and bases is far more complicated than that of amino-acids outlined above.

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^{1} These changes can be represented as follows in terms of the older formulæ:

Addition of acid ; $H_2N.CHR.COOH + H^+ \;=\; ^+H_3N.CHR.COOH$ (C)
$\text{(uncharged molecule; neutral)} \qquad\qquad \text{(cation)}$

Addition of alkali ; $H_2N.CHR.COOH \;+\; OH^-$
$\text{(uncharged molecule; neutral)}$
$\qquad\qquad =\; H_2N.CHR.COO^- + HOH$ (D)
$\qquad\qquad\qquad \text{(anion)}$
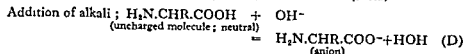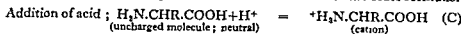
of protein structure, showing peptide linkages and side-chains containing various substituent radicals :

†H$_2$N.CH$_2$.CO.NH.CH.CO ..... NH.CH.CO.NH.CH.COOH*

| | (CH$_2$)$_2$ | large | (CH$_2$)$_4$ | CH$_2$ |
| | COOH* | number of amino-acid units | NH$_2$† | C$_6$H$_4$OH§ |
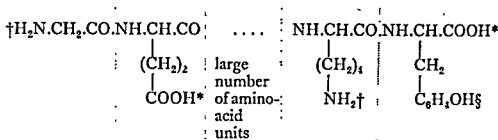
This on hydrolysis would yield

glycine : glutamic : etc., etc. : lysine : tyrosine
              acid

* The side-chain carboxyl radical of the glutamic acid and the carboxyl radical at the end of the chain confer acidic properties on the molecule.

† The side-chain amine radical of the lysine and the amine radical at the end of the chain confer basic properties on the molecule.

§ The phenolic radical of tyrosine confers certain phenolic properties on this protein molecule (e.g., the latter gives Millon's test).

Some proteins contain constituents other than amino-acids, e.g., haem, a complex heterocyclic compound which is a constituent of the haemoglobin molecule. The classification of proteins is difficult, and will not be considered here. Some classes (e.g., albumins, globulins) may be disper............
colloidal solut
particles are ....
gels. Certain other proteins (e.g., keratin) are insoluble in nearly all aqueous solutions.

The reactions of amino-acids and proteins are here grouped into four classes as follows :

1. *General Reactions of Amino-acids* (Section 14, 18, pp. 400-402).

These are the expected reactions of compounds containing both amino and carboxyl radicals.

2. *General Reactions of Proteins* (Section 14, 19, pp. 402-407).

These are chiefly the expected reactions of amphoteric colloidal electrolytes.

3. *Reactions of Particular Amino-acids* (Section 14, 20, pp. 408-409).

These reactions depend on the presence of radicals other than amino and carboxyl in certain amino-acids ; most of them are given by these amino-acids both when free and when combined in proteins. Some of the reactions (e.g., xanthoproteic and Millon's tests) have been met already in the " grammar " of organic chemistry in Chapter 12. Others (e.g., Sakaguchi's test) depend on the presence of radicals not previously encountered.

scratching the side of the tube after each drop has been added. Note that when the colour of the indicator is orange to yellow ($pH=5$-6) a white precipitate is formed. This redissolves when the colour of the indicator changes to green ($pH=8$).

2. Formation of Characteristic Salts.

The copper salts of amino-acids are deep-blue coloured substances, many of them sparingly soluble in water. The blue colour is probably due to co-ordination of the NH_2 radicals with copper. (Compare the cuprammonium ion, pp. 80-81, 87.)

> To glycine (0·5M solution, 1 ml.) add copper sulphate solution (5 drops); a deep-blue colour is produced. Carry out a control test with water instead of glycine solution.

Many amino acids form characteristic sparingly-soluble salts with picric acid and other complex acids.

3. Condensation with Formaldehyde.

The amino radicals of amino-acids condense with formaldehyde thus:

$$H_2C:O+H_3N.CHR.COO^- = H_2C:N.CHR.COOH+H_2O.$$

(Compare general reactions of carbonyl compounds, p. 330.)

In the condensation products the amino radicals have been masked, and the nitrogen atoms are no longer basic. The amino-acids when treated with formaldehyde are therefore transformed from neutral into acidic substances and can be titrated with alkali. This reaction forms the basis of Sörensen's method for titrating amino-acids.

The method is used for following the breakdown of proteins *in vitro* or their digestion in the alimentary canal. When the peptide links in proteins are broken by hydrolysis, amino and carboxyl radicals are produced in equal numbers and the solution becomes neither more acid nor more alkaline.

$$\begin{array}{ccc} X.C:O & & X.COOH \\ | & \rightarrow & + \\ Y.N.H & & Y.NH_2 \end{array}$$
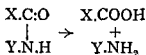
If the products are now treated with formaldehyde, the amino radicals condense with this:

$$\begin{array}{ccc} X.COOH & & X.COOH \\ + & & + \\ Y.NH_2+O:CH_2 & & Y.N:CH_2 \end{array}$$
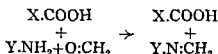
The solution then becomes acid and titration with alkali determines the number of peptide links which have been broken.

> Take glycine (0·5M solution, 5·0 ml.), add phenolphthalein (2 drops) and then sodium hydroxide (1·0M) until the solution is *faintly* pink. Take formalin (2·0 ml.), add phenolphthalein

The protein when electrically neutral (*i.e.*, at its iso-electric point) may be represented as a mixture of uncharged molecules $H_2N.X.COOH$ and dipolar ions $^+H_3N.X.COO^-$.

At pH values above and below its iso-electric point the protein exists as anions $H_2N.X.COO^-$ and cations $^+H_3N.X.COOH$ respectively. The changes which take place on the additions of acid or base to a protein may be represented by equations similar to (A) or (C) and (B) or (D) respectively. The iso-electric points of some proteins are as follows:

egg-albumin, 4·6; caseinogen, 4·7; haemoglobin, 6·8.

(For an experiment on the iso-electric point of a protein, see p. 403).

Many precipitations and staining reactions of proteins may be explained crudely in terms of the above ideas on the charges carried by proteins in solutions of different pH (for explanations and details of experiments, see pp. 403-406).

MATERIALS FOR EXPERIMENTS

The materials used to illustrate the reactions are as follows :

Amino-acids—glycine, tyrosine.

Proteins—egg-albumin solution, blood plasma (containing serum albumin, serum globulin and fibrinogen), caseinogen solution, gelatin solution (gelatin is not a native but a derived protein), diluted ox-blood.

14, 18   AMINO-ACIDS, GENERAL REACTIONS

The general reactions of amino-acids are chiefly those expected of compounds containing $.NH_2$ and $.COOH$ radicals.

1. Acidic and Basic Properties.

Amino-acids are amphoteric electrolytes. Their behaviour in solutions of varying pH is discussed on pp. 399-400. The monoamino-monocarboxylic acids ($^+H_3NCHR.COO^-$) form solutions in water which are almost neutral. (Test the given 0·5M solution of glycine.) Tyrosine (*p*-hydroxyphenylalanine $HO.C_6H_4.CH_2.CH(NH_3^+)COO^-$) illustrates well the amphoteric properties of amino-acids since it is almost insoluble in water at its iso-electric point, but is readily "soluble" in more acid or more alkaline solutions.

The amino-acid is dissolved in a strong acid and caustic alkali is gradually added. When the pH of the solution reaches the iso-electric point of tyrosine the latter is precipitated. When the pH is raised above the iso-electric point, the tyrosine dissolves again.

> Dissolve tyrosine (0·1 g.) in dilute hydrochloric acid (10 drops) and add Universal Indicator (1 drop of a 1-in-10 dilution). Add dilute sodium hydroxide dropwise from a pipette, shaking and

and sodium chloride. The latter dialyses through a membrane of parchment-paper, the former does not.

2. Carry out the experiment as detailed for starch and sodium chloride on pp. 170-171. Test for protein by the biuret test.

The Iso-Electric Point.

The solubilities of proteins are minimal at their iso-electric points and certain proteins are easily precipitated at their iso-electric points. The precipitates can be redissolved by altering the pH of the liquid. For a discussion of the reactions taking place, see pp. 399-400.

The iso-electric point of a protein which is insoluble at this point can be determined as follows : A solution of the protein at a pH above the iso-electric point is taken and to separate samples of this solution are added increasing quantities of a strong acid. The pH values of the samples are determined ; that of the sample containing the largest precipitate is nearest to the iso-electric point of the protein.

3. Take in each of seven test-tubes 5 ml. of the given solution of caseinogen (0·6% in 0·02M aqueous sodium acetate). To these tubes add respectively 0, 0·5, 1·0, 1·5, 2·0, 2·5, 3·0 ml., 0·1M hydrochloric acid. Mix the solution in each tube by inverting, not shaking ; note the amount of precipitate (if any) in each tube and add to each tube Universal Indicator (1 drop). Compare the colorations obtained with the set of standards in the laboratory and deduce the pH of each solution. The liquid containing the largest precipitate is nearest to the iso-electric point of caseinogen. Tabulate your observations and conclusions.

The insolubility of certain native and derived proteins at their iso-electric points serves for their detection and separation from aqueous solution. One of the common tests for albumin in urine depends on the precipitation of metaprotein (see p. 407) at its iso-electric point.

PRECIPITATION BY CERTAIN CATIONS AND ANIONS

The molecules of proteins in solution on the alkaline side of their iso-electric points are colloidal anions, and form insoluble " salts " with certain polyvalent cations (e.g., Fe^{+++}, Hg^{++}, Zn^{++}, Pb^{++}).

$$3H_2N.X.COO^- + Fe^{+++} = [(H_2N.X.COO)_3Fe].$$
$$\text{(anion)} \qquad\qquad \text{(neutral; insoluble)}$$
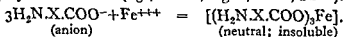
In some cases the precipitated protein dissolves on further addition of positive ions of the same kind. This is probably due to a reversal of charge on the protein molecule.

$$3H_2N.X.COO^- + 2Fe^{+++} = [(H_2N.X.COO)_3Fe_2]^{+++}.$$
$$\text{(anion)} \qquad\qquad \text{(cation ; goes into colloidal}$$
$$\text{solution again)}$$
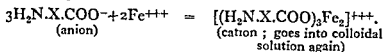
The use of heavy metal salts as astringents and antiseptics depends on their power of .... typtics

When the proteins .... their

(2 drops) and again add sodium hydroxide (1·0M) until the solution is faintly pink. Now add the formalin solution to the glycine solution. The mixture becomes colourless, as free carboxyl radicals are now present. Titrate with sodium hydroxide (1·0M) from a graduated pipette to a pale pink colour. Compare the volume of sodium hydroxide used with that calculated from the above equations.

4. Reaction with Nitrous Acid.

The amino radicals of amino-acids undergo the usual reaction with nitrous acid, nitrogen being evolved.

$$HON{:}O + {}^{+}H_3N.CHR.COO^{-} = HO.CHR.COOH + N_2 + H_2O.$$

This reaction forms the basis of the important Van Slyke method for the determination of amino radicals in protein hydrolysates.

Carry out the reaction as instructed on p. 348, using a solution of glycine (0·5M, 2 ml.) instead of methylamine hydrochloride.

5. Ninhydrin Reaction.

Ninhydrin (triketohydrindene hydrate) gives with amino-acids (and with peptides and proteins) a deep-blue colour. The chemistry of the reaction is complicated.

To glycine (0·5M solution, 1 ml.) add ninhydrin solution (2 drops) and boil. A blue colour is slowly produced.

14, 19   REACTIONS OF THE PROTEIN MOLECULE AS A WHOLE

PROTEINS AS POLYPEPTIDES

The Biuret Test.

This reaction is given by any substance containing two —CO.NH— groups joined in one of the following ways : (a) joined directly, as in oxamide; (b) joined by a nitrogen atom, as in biuret (see reactions of urea, p. 425); (c) joined by a carbon atom, as in malonamide, in proteins and in the partial breakdown products of the latter. The reaction is not given by the individual amino-acids (or by dipeptides).

1. To egg-albumin solution (2 ml.) add dilute sodium hydroxide solution (2 ml.) followed by copper sulphate solution (1 drop, not more). A pink or violet colour is formed. Carry out a blank test with water.

PROTEINS AS AMPHOTERIC COLLOIDAL ELECTROLYTES

Colloidal Nature of Proteins.

The colloidal nature of aqueous solution of proteins may be demonstrated by dialysis, using an aqueous solution containing egg-albumin

These properties are illustrated below by the staining reactions of rabbit-wool (largely keratin). Many stains used in histological work are acidic or basic dye-stuffs and therefore stain only basic or acidic constituents of the tissues. Certain stains which contain both an acidic and a basic dye-stuff (e.g., Leishman's or Giemsa's stains, which are mixtures of eosin and methylene blue) serve a dual purpose, since they stain acidic and basic materials in different colours. They are used in staining blood films for differential leucocyte counts.

5. In each of four test-tubes (I, II, III, IV) take a pinch of white rabbit-wool. Then make further additions as follows :

Tube	I	II	III	IV
Glacial Acetic Acid (drops) .	5	5	o	o
Concentrated Ammonia (drops)	o	o	5	5
Eosin Solution (ml.) . .	5	o	o	5
Methylene Blue Solution (ml.) .	o	5	5	o

Mix the contents of each tube and allow to stand for five minutes, decant the liquids, and wash each sample of wool four times with water in the tube. The final colours of the wool should be as follows :

I, pink ; II, white ; III, blue ; IV, white.

The reactions (if any) taking place are represented by the equations I, II, III, IV above.

CO-PRECIPITATION WITH OTHER COLLOIDS

Colloids of opposite sign precipitate one another, e.g., arsenious sulphide (negative) and ferric hydroxide (positive) (see pp. 126-127, 172).

Mutual precipitation takes place when negatively-charged proteins (i.e., proteins in solution on the alkaline side of their iso-electric points) are mixed with colloidal ferric hydroxide in appropriate quantities.

$$[H_2N.X.COO]^- + [Fe(OH)_3]^+ = [(H_2N.X.COO)(Fe(OH)_3)].$$
$$\text{(neutral ; insoluble)}$$

If an excess of ferric hydroxide is added, no precipitation takes place, presumably because the charge on the protein molecule is reversed.

$$[H_2N.X.COO]^- + 2[Fe(OH)_3]^+ = [(H_2N.X.COO)2Fe(OH)_3]^+.$$
$$\text{(cation ; goes into colloidal solution again)}$$

iso-electric points they are colloidal cations, and form insoluble salts with various anions (mainly complex ones). The reagents used are trichloroacetic, picric, tannic, and salicylsulphonic [1] acids.

If the protein is on the alkaline side of its iso-electric point, the addition of acid first turns it from an anion to a cation.

$$H_2N.X.COO^- + 2H^+ \ \rightleftharpoons \ ^+H_3N.X.COOH.$$
$$\text{(anion)} \quad \text{(from acid)} \qquad \text{(cation)}$$
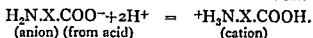
The cation then combines with the anion of the acid, thus:

$$^+H_3N.X.COOH + CCl_3COO^- \ = \ [(^+H_3N.X.COOH)(CCl_3COO^-)].$$
$$\text{(neutral; insoluble)}$$
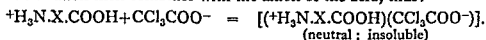
If a salt of one of these acids is added to the protein in the alkaline side of its iso-electric point, there is no precipitation.

$$H_2N.X.COO^- + CCl_3.COO^- \ \textit{cannot combine.}$$
$$\text{(anion)} \qquad \text{(anion)}$$

Precipitation tests are used for the detection and approximate determination of albumin in urine (salicylsulphonic acid test for detection; Esbach's method, using picric acid, for determination). The treatment of burns with tannic acid consists essentially in the formation of an impermeable protein-tannate from the damaged tissue-proteins.

4. To separate portions of egg-albumin solution (2 ml. each)
. . . .

. . . .

acid (or picric acid or tannic acid or salicylsulphonic acid); (c) sodium trichloroacetate.

STAINING OF PROTEINS

Their behaviour towards acidic and basic dye-stuffs illustrates well the amphoteric nature of proteins.

Suppose HA and BOH represent acidic and basic dye-stuffs respectively. A protein on the acid side of its iso-electric point is present as cations $^+H_3N.X.COOH$. If the protein in this condition is treated with a dye-stuff HA, e.g., eosin, combination with the anions of the latter may take place, and the protein may be stained.

$$^+H_3N.X.COOH + A^- \ = \ [^+H_3N.X.COOH.A^-] \qquad . \qquad . \quad I$$

If the protein is treated with a basic dye-stuff BOH, e.g., methylene blue, combination cannot take place and the protein is not stained.

$$^+H_3N.X.COOH + B^+ \ \textit{cannot combine} \qquad . \qquad . \qquad . \quad II$$

Conversely, a protein on the alkaline side of its iso-electric point is present as anions $H_2N.X.COO^-$, and will combine with the cations of the basic dye-stuff BOH but not with an acidic dye-stuff.

$$H_2N.X.COO^- + B^+ \ \rightleftharpoons \ [H_2N.X.COO^-.B^+] \qquad . \qquad . \quad III$$
$$H_2N.X.COO^- + A^- \ \textit{cannot combine} \ (\text{will not stain}) \qquad . \quad IV$$
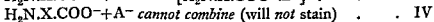
[1] Also called sulphosalicylic acid or 2-carboxyphenol-4 sulphonic acid.

These properties are illustrated below by the staining reactions of rabbit-wool (largely keratin). Many stains used in histological work are acidic or basic dye-stuffs and therefore stain only basic or acidic constituents of the tissues. Certain stains which contain both an acidic and a basic dye-stuff (*e.g.*, Leishman's or Giemsa's stains, which are mixtures of eosin and methylene blue) serve a dual purpose, since they stain acidic and basic materials in different colours. They are used in staining blood films for differential leucocyte counts.

5. In each of four test-tubes (I, II, III, IV) take a pinch of white rabbit-wool. Then make further additions as follows:

Tube	I	II	III	IV
Glacial Acetic Acid (drops) .	5	5	0	0
Concentrated Ammonia (drops)	0	0	5	5
Eosin Solution (ml.) . .	5	5	0	5
Methylene Blue Solution (ml.) .	0	5	5	0

Mix the contents of each tube and allow to stand for five minutes, decant the liquids, and wash each sample of wool four times with water in the tube. The final colours of the wool should be as follows:

I, pink; II, white; III, blue; IV, white.

The reactions (if any) taking place are represented by the equations I, II, III, IV above.

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Colloids of opposite sign precipitate one another, *e.g.*, arsenious sulphide (negative) and ferric hydroxide (positive) (see pp. 126-127, 172).

Mutual precipitation takes place when negatively-charged proteins (*i.e.*, proteins in solution on the alkaline side of their iso-electric points) are mixed with colloidal ferric hydroxide in appropriate quantities.

$$[H_2N.X.COO]^- + [Fe(OH)_3]^+ = [(H_2N.X.COO)(Fe(OH)_3)].$$
$$\text{(neutral ; insoluble)}$$

If an excess of ferric hydroxide is added, no precipitation takes place, presumably because the charge on the protein molecule is reversed.

$$[H_2N.X.COO]^- + 2[Fe(OH)_3]^+ = [(H_2N.X.COO)2Fe(OH)_3]^+.$$
$$\text{(cation ; goes into colloidal solution again)}$$

6. In each of 7 test-tubes place egg-albumin solution (5 ml.). To these tubes add respectively 0, 0·5, 1·0, 1·5, 2·0, 2·5, 3·0 ml. colloidal ferric hydroxide solution. Mix the contents of each tube by inverting, fill nearly to the top with water and mix again. Note the appearance after half an hour and tabulate your observations.

PRECIPITATION BY DEHYDRATION

Hydrophilic colloids are precipitated from their solutions by the addition of substances which have a greater affinity for water, *e.g.*, neutral salts in high concentration and ethyl alcohol (see pp. 124-126).

All the chief classes of proteins are precipitated by saturation of their solutions with ammonium sulphate. While most proteins are precipitated by half-saturation with ammonium sulphate, the *albumins* are not precipitated by this treatment. The albumins and globulins of serum can therefore be separated by half-saturation with ammonium sulphate, filtration, and complete saturation of the filtrate with ammonium sulphate. Precipitates obtained in this way can be redissolved, the *albumins in pure water, the globulins in dilute aqueous salt* solutions.

The proteins appear to be unchanged in nature by this precipitation. In the experiment below, gelatin is used as an example of a protein which is precipitated by half-saturation, since globulins are difficult to obtain pure.

Albumins and globulins are precipitated from their solutions by ethyl alcohol. If the precipitated proteins are treated immediately with water, they redissolve. If, however, they are left in contact with ethyl alcohol for an hour, they are "denatured" (see p. 407), and are no longer soluble in water.

Precipitation by half-saturation with ammonium sulphate is used in testing for excess of globulin in cerebrospinal fluid.

7. Charge six test-tubes as follows:

Tube	I	II	III	IV	V	VI
Egg - albumin solution (ml.) .	2	2	2	0	0	0
Gelatin solution (ml.) .	0	0	0	2	2	2
Water (ml.) . .	8	3	0	8	3	0
Satd. $(NH_4)_2SO_4$ solution (ml.) .	0	5	8	0	5	8
Solid $(NH_4)_2SO_4$	*Nil*	*Nil*	*	*Nil*	*Nil*	*

* Sufficient to saturate solution (some solid must remain undissolved).

Mix the contents of each tube thoroughly without shaking and note the results. Precipitates are formed in tubes III, V, and VI only. Dilute the mixture from each of these tubes to about 100 ml. with water. The precipitates redissolve.

DENATURATION

Albumins and globulins may be transformed by heat, by various reagents (*e.g.*, nitric acid, ethyl alcohol, urea, phenol), or by surface forces (*e.g.*, when an aqueous solution is shaken with air) into less soluble substances called *denatured proteins* or *metaproteins*. The changes in the character of the protein probably differ according to the type of treatment used, and are usually irreversible.

Denatured albumins differ from native albumins in that they are insoluble at their iso-electric points. Thus if denaturation is carried out at or near the iso-electric point of the metaprotein, a precipitate or coagulum is immediately formed. If, however, the pH of the solution is not at the iso-electric point, no immediate precipitation takes place, but the metaprotein can be precipitated by adjusting the pH of the solution to this point. The metaproteins are soluble only in strongly acidic or alkaline solutions.

The formation of insoluble denaturation-products from proteins forms the basis of tests for these in urine and cerebrospinal fluid. The tests used on urine involve the denaturation and precipitation of albumin by *heat* or by *concentrated nitric acid*. A test used on cerebrospinal fluid involves the denaturation and precipitation of globulin by *phenol*.

8. *Heat Denaturation.*

Heat diluted blood plasma (2 ml.) or egg-albumin solution (2 ml.) slowly to boiling. The solution becomes cloudy. Cool and add acetic acid (0·1M) dropwise. A white precipitate is formed and redissolves on the addition of further acid.

9. *Denaturation by Ethyl Alcohol.*

To egg-albumin solution (2 ml.) add ethyl alcohol (4 ml.). A white precipitate is formed. Allow this to stand for an hour and show that it is then insoluble in water, but " soluble " in dilute acetic acid or dilute sodium hydroxide.

10. *Denaturation by Nitric Acid.*

Take concentrated nitric acid (2 ml.) in a test-tube and run on to it egg-albumin solution (2 ml.) from a pipette. A white ring of metaprotein is formed at the interface.

14, 20 REACTIONS OF PARTICULAR AMINO-ACIDS

Unless otherwise stated these reactions are given by the amino-acids both when free and when combined in proteins.

<center>AROMATIC AMINO-ACIDS</center>

1. Xanthoproteic Test.

The amino-acids containing aromatic nuclei (phenylalanine, tyrosine, tryptophane), on heating with nitric acid, give yellow acidic polynitro compounds, which in alkaline solution yield orange anions. (Compare general reactions of the aromatic nucleus, pp. 318–319.)

> To the protein solution (*e.g.*, egg-albumin, 2 ml.) add concentrated nitric acid (1 ml.). A white precipitate of metaprotein is formed. Boil for half a minute ; the precipitate turns yellow. Cool and make alkaline with ammonia ; the precipitate turns orange.

<center>CYSTINE AND CYSTEINE</center>

2. Lead Test.

Cystine ($HOOC.CH(NH_2).CH_2.S)_2$ and cysteine ($HOOC.CH(NH_2)$ CH_2SH), two of the three sulphur-containing amino-acids of proteins, are *hydrolysed by concentrated caustic alkali, giving sulphide ions* which may be detected by the formation of lead sulphide (see p. 249). Methionine ($HOOC.CH(NH_2).CH_2.CH_2.SCH_3$) is *not* hydrolysed in these conditions. A yellow or brown colour indicates the presence of cystine or cysteine in the original material. Egg-albumin contains cystine, gelatin does not. Carry out the following test with solutions of these two substances:

> To the protein solution (2 ml.) add sodium hydroxide (20% aqueous solution, 2 ml.) and boil for two minutes. Cool and add sodium plumbite solution (1 drop).

<center>ARGININE</center>

3. Sakaguchi's Test.

. . . . taining
. . . . hol and
. . . .

> To the protein solution (*e.g.*, egg-albumin, 2 ml.) add dilute sodium hydroxide solution (1 ml.), α-naphthol (*alcoholic solution*, 2 drops) and sodium hypochlorite solution (1 drop) and mix. A red colour develops slowly.

TYROSINE

4. Millon's Test.

Phenols with Millon's reagent give red colours (see p. 325). The only phenolic amino-acid in proteins is tyrosine (*p*-hydroxyphenylalanine).

To the protein solution (*e.g.*, egg-albumin, 2 ml.) add Millon's reagent (2 ml.). A white precipitate is formed. Heat in the boiling water bath for two minutes. If tyrosine is present a brick-red colour is produced.

TRYPTOPHANE

5. Aldehyde Test.

Tryptophane (β-indolylalanine, formula below) condenses with aldehydes in the presence of concentrated sulphuric acid and an oxidising agent (*e.g.*, mercuric sulphate) to give purple products.
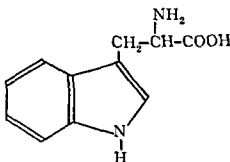
Tryptophane

Carry out the following test with egg-albumin which contains tryptophane, and gelatin which does not :

To the protein solution (1 ml.) add formaldehyde solution (0·1%, 1 drop). Then add mercuric sulphate solution (10%, 1 drop) and mix. Add concentrated sulphuric acid (1 ml.) and mix again by gentle shaking. If tryptophane is present a purple colour is produced.

6. Bromine Test.

Free tryptophane yields with bromine water a purple product which is extracted from aqueous solution by butyl alcohol. Tryptophane units in a protein molecule do *not* give this purple colour.

To a solution of tryptophane (2 ml.) add glacial acetic acid (1 drop). Then add dilute bromine water dropwise until further addition does not cause a deepening of the purple colour. (If excess bromine water is added, the purple colour is destroyed.) Shake the solution with butyl alcohol (1 ml.). The colour is extracted by this solvent.

14, 20 REACTIONS OF PARTICULAR AMINO-ACIDS

Unless otherwise stated these reactions are given by the amino-acids both when free and when combined in proteins.

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CYSTINE AND CYSTEINE

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Cystine $(HOOC.CH(NH_2).CH_2.S)_2$ and cysteine $(HOOC.CH(NH_2) CH_2SH)$, two of the three sulphur-containing amino-acids of proteins, are hydrolysed by concentrated caustic alkali, giving sulphide ions which may be detected by the formation of lead sulphide (see p. 249). Methionine $(HOOC.CH.NH_2.CH_2.CH_2.SCH_3)$ is *not* hydrolysed in these conditions. A yellow or brown colour indicates the presence of cystine or cysteine in the original material. Egg-albumin contains cystine, gelatin does not. Carry out the following test with solutions of these two substances:

> To the protein solution (2 ml.) add sodium hydroxide (20% aqueous solution, 2 ml.) and boil for two minutes. Cool and add sodium plumbite solution (1 drop).

ARGININE

3. Sakaguchi's Test.

> To the protein solution (e.g., egg-albumin, 2 ml.) add dilute
> ⋯ ml.), α-naphthol (alcoholic solution,
> hlorite solution (1 drop) and mix.

Compounds containing   *Compounds containing*
ferrous iron   *ferric iron*

Oxyhaemoglobin   **Carboxyhaemo-**
                                 globin

high O₂ pressure | low O₂ pressure (a)   (a) CO
                                              oxidising agents
Haemoglobin ←————————————————————→ **Methaemoglobin**
                              reducing agents
                                 (b)
                                                      (d)
          (c)   acetic acid +
          denaturation   sodium chloride

Haemochromogen
(of denatured globin)

                                    → **Haemin** (chloride of
                                                  oxidised haem)*
   (d) acetic acid
       +sodium chloride
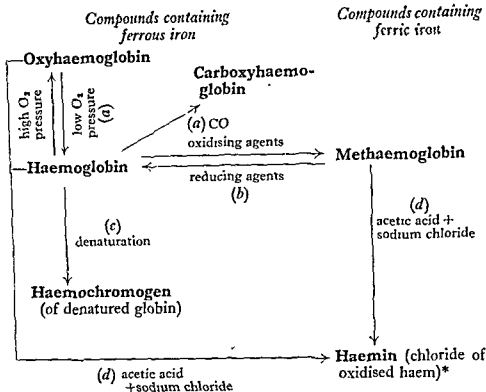
* Together with decomposition products of globin.

The other two reactions are the liberation of iron (1), and the benzidine reaction (8). The latter depends on the fact that haemoglobin acts as a peroxidase, *i.e.*, it enables hydrogen peroxide to oxidise certain organic compounds, including benzidine (an aromatic diamine, $H_2N.C_6H_4.C_6H_4.NH_2$) which yields a highly-coloured quinonoid product.

Haem derivatives are usually distinguished by their colours as seen by the naked eye or by their absorption spectra. If white light is passed through a coloured substance or solution, light of certain wave-lengths is absorbed; if the light is then spread out into a spectrum the wave-lengths which have been absorbed are indicated by black bands. The spectra of the compounds considered here are illustrated in Fig. 14, 3, facing p. 412.

REACTIONS

Use defibrinated ox-blood for these reactions.

Adjustment of the Spectroscope.

Pocket spectroscopes are adjusted as follows: A sodium flame is produced by placing a few crystals of sodium chloride on a wire gauze and heating them with a Bunsen burner. The eye-piece of the spectroscope is then focussed on the slit, using the light of the sodium flame. The slit is then narrowed until the yellow line almost disappears. This

14, 21 REACTIONS OF NON-AMINO-ACID CONSTITUENTS AND OF PROTEINS CONTAINING THEM

A. HAEMOGLOBIN AND RELATED SUBSTANCES

The pigment of vertebrate red blood corpuscles, haemoglobin, is a conjugated protein consisting of a protein *globin* and a non-protein component *haem*. Haem is a compound containing four pyrrole nuclei linked to form the skeleton shown below (called the *porphin* skeleton) and one atom of iron. The presence of iron in haemoglobin may be demonstrated in the laboratory (see reaction 1). The physiological importance of haemoglobin lies chiefly in its power to form an easily dissociable molecular complex with oxygen which plays an essential part in the transport of oxygen from the lungs to the tissues.
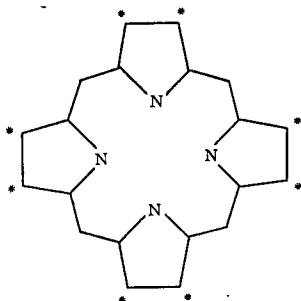
Porphin Nucleus

All angles except those marked N are occupied by carbon-atoms. The bonds round the ring are alternately double and single. Haem and related substances have substituents at the points marked *. The iron atom of haem is linked to all four nitrogen-atoms.

The reactions of haemoglobin and related compounds considered here are, with two exceptions, summarised in the following table. These reactions are of four types, viz. :

(a) formation of molecular addition-compounds (dissociable or not) ;

(b) oxidation of ferrous to ferric iron, or reduction of ferric to ferrous iron ;

(c) denaturation of globin ;

(d) splitting of haem from globin.

WAVE-LENGTHS (in mμ)

400   500   600   700

Reduced
Haemoglobin

Oxyhaemoglobin

Carboxy-
haemoglobin

Haemo-
chromogen

Methaemoglobin

VIOLET   BLUE   GREEN | RED
YELLOW ORANGE
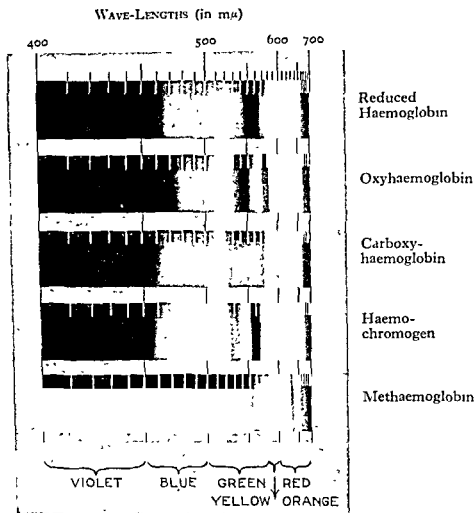
(By permission of Messrs. J. and A. Churchill, Ltd)

FIG. 14, 3

Absorption Spectra of Haemoglobin
and its Derivatives

results in the production of a weaker but purer spectrum when white light is analysed by the spectroscope.

1. Presence of Iron in Blood.

The organic matter in blood is destroyed by heating with concentrated sulphuric and nitric acids, and the presence of iron in the residue is demonstrated by means of thiocyanate.

> Heat blood (2 drops) with concentrated sulphuric acid (2 ml.) and concentrated nitric acid (1 ml.) until a clear yellow solution is obtained. Cool and pour this into water (10 ml.). To the resulting solution (2 ml.) add potassium thiocyanate solution (2 drops). A red colour, due to ferric thiocyanate, is produced.

2. Oxyhaemoglobin.

Reduced haemoglobin may be converted to oxyhaemoglobin by shaking with air or oxygen. The spectrum of oxyhaemoglobin shows two bands in the green. Oxyhaemoglobin is red in concentrated and yellow in dilute solution.

> Dilute blood (2 drops) with water (5 ml.) and shake vigorously. The solution is red. Examine and draw its absorption spectrum. Then dilute the solution (2 ml.) to 20 ml. with water ; the colour changes to yellow, but the absorption spectrum remains the same.

3. Reduced Haemoglobin.

Oxyhaemoglobin may be converted to reduced haemoglobin by exposing it to a vacuum or by treating it with sodium hydrosulphite ($Na_2S_2O_4$). Reduced haemoglobin is purple both in concentrated and dilute solution ; its spectrum shows a single band in the green.

> Dilute blood (2 drops) with water (5 ml.). Add sodium hydrosulphite ($\frac{1}{10}$ spatula-point) and mix gently without shaking with air. The colour changes to purple. Examine and draw the absorption spectrum of the solution. Divide the solution into two equal parts. Shake one part vigorously with air. The colour changes to red again as oxyhaemoglobin is formed. (Examine its spectrum.) Dilute the other part to 20 ml. with water ; the colour remains purple.

4. Carboxyhaemoglobin.

Haemoglobin combines with carbon monoxide to give a complex (carboxyhaemoglobin) which is *not* readily dissociable (contrast oxyhaemoglobin). Carboxyhaemoglobin is formed when coal gas is inhaled, and since it is not readily dissociable the haemoglobin thus combined is useless for respiratory purposes. Carboxyhaemoglobin is bright scarlet in concentrated and pink in dilute solutions. Its absorption spectrum contains two bands of slightly shorter wave-length than the bands of oxyhaemoglobin. Carboxyhaemoglobin and oxyhaemoglobin can be distinguished spectroscopically by more elaborate instruments, but not by the simple pocket spectroscope.

ALCOHOLS

Ethyl alcohol (" alcohol " or " spirit ") is used as an antiseptic and in the preparation of liniments, lotions and tinctures.

The following grades of alcohol may be met. The impurities in the two kinds of methylated spirit are added deliberately to make the alcohol unfit for drinking.

Absolute Alcohol. This should be 100% ethyl alcohol; most samples contain 1-2% water.

Rectified Spirit. Contains approximately 95% ethyl alcohol and 5% water.

Industrial Methylated Spirit. Contains approximately 95% ethyl alcohol and 5% crude wood spirit (mainly methyl alcohol); used as an antiseptic.

"Mineralised" Methylated Spirit. Contains approximately 90% ethyl alcohol, 9% wood spirit, and traces of pyridine, naphtha and methyl violet.

PHENOLS

Phenol itself (" carbolic acid "), and many other members of the phenol class, are used as antiseptics.

ETHERS

Diethyl ether (" ether ") is used as a general anaesthetic. Care must be taken to ensure that ether used for anaesthesia and for many chemical purposes is free from *peroxides*, which may be detected by the production of a blue colour with potassium iodide and starch. Peroxides may be removed by washing the ether with ferrous sulphate solution. Their formation may be prevented by storing ether in dark bottles with a minimum of air-space and containing a piece of copper wire projecting above the surface of the ether. (The mode of action of the copper wire is not understood.)

Ether containing some ethyl alcohol and water is used where a less pure material is satisfactory—*e.g.*, for cleaning skin. This is referred to as " Methylated Ether " or " Ether Meth", since it is prepared from industrial methylated spirit.

ESTERS

None of the four esters mentioned in p. 341 is of medical importance, but benzyl benzoate ($C_6H_5.COO.CH_2.C_6H_5$) is used in the treatment of scabies.

AMINES

Some quaternary ammonium salts containing long-chain alkyl radicals (*e.g.*, cetyltrimethylammonium bromide, " Cetavlon," $C_{16}H_{33}N(CH_3)_3{}^+.Br^-$) are used as disinfectants and detergents (see p. 122).

ALKYL HALIDES

Ethyl chloride is used as an anaesthetic both general and local.

... over a very small flame until the acetic acid begins to boil.

Remove from the flame, run another drop of acetic acid under the cover-slip, and examine under the microscope.

2. Sensiline Test.

... ...

... a solution of benzidine in glacial acetic acid (1 ml.) and hydrogen peroxide (two volumes, 1 ml.). Then add one drop of a ... ... solution of blood and allow to stand. The solution slowly becomes green and then deep blue.

22. REACTIONS OF NON-AMINO-ACID CONSTITUENTS AND OF PROTEINS CONTAINING THEM

1. PHOSPHATE AND CARBOHYDRATE

Molybdate Test for Phosphate.

Certain proteins contain phosphate radicals which esterify the hydroxyl groups of certain ... (hydroxyamine, $HOCH_2CH(NH_3^+)COO^-$) ... . The presence of phosphate may be demonstrated by destroying the organic part of the molecule with concentrated sulphuric and nitric acids and applying the molybdate test (see p. 236) to the product.

Heat casinogen (1 spatula-point), concentrated sulphuric acid (1 ml.) and concentrated nitric acid (1 ml.) carefully until a clear solution is obtained. Cool this, and pour it into water (5 ml.). To the resulting solution (2 ml.) add ammonium molybdate solution (10 drops) and warm. A yellow precipitate of ammonium phosphomolybdate is obtained.

Molisch Test for Carbohydrate.

Many proteins contain carbohydrate units in their molecules, and therefore give a positive result in the Molisch test.

Carry out the Molisch test as detailed on p. 392 with solutions of ovalbumin (which contains carbohydrate) and gelatin (which does not).

MISCELLANEOUS COMPOUNDS

23. MEDICAL USES OF SIMPLE COMPOUNDS DISCUSSED IN CHAPTER 12

HYDROCARBONS

Liquid paraffin (used as a lubricant in constipation) and vaseline (used as an emollient) consist chiefly of mixed paraffin hydrocarbons. Cyclopropane $(CH_2)_3$, a non-aromatic cyclic hydrocarbon, is used as a general anaesthetic.

ALCOHOLS

Ethyl alcohol (" alcohol " or " spirit ") is used as an antiseptic and in the preparation of liniments, lotions and tinctures.

The following grades of alcohol may be met. The impurities in the two kinds of methylated spirit are added deliberately to make the alcohol unfit for drinking.

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ALKYL HALIDES

Ethyl chloride is used as an anaesthetic both general and local.

14, 24   **CHLOROFORM**

Chloroform, $CHCl_3$, is a liquid (b.p. 61°, $d=1·50$). It is almost immiscible with water (100 ml. water dissolve 1 g. $CHCl_3$), but miscible in all proportions with alcohol or ether.

Its chemical properties are chiefly those expected of a polyhalogen compound (compare pp. 353–354). It is important in medicine as an anaesthetic[1] and in organic chemistry as a solvent for non-hydroxylic compounds (*e.g.*, lipoids). Chloroform for use in anaesthesia must be free from the poisonous phosgene ($COCl_2$), which is formed if chloroform is allowed to stand in air and light. Anaesthetic chloroform is kept in dark bottles and contains a little ethyl alcohol which inhibits the formation of phosgene.

<p style="text-align:center">REACTIONS</p>

1. Covalent Nature.

The C–Cl bonds are covalent; no precipitate is therefore formed with silver nitrate.

> Shake chloroform (5 drops) with bench silver nitrate solution (2 ml.). No precipitation of silver chloride occurs.

2. Hydrolysis by Alkali.

Chloroform is hydrolysed by caustic alkali to alkali metal chloride and formate

$$HCCl_3 + 4OH^- = HCOO^- + 3Cl^- + 2H_2O.$$

The chloride, which is now ionised, gives a precipitate with silver nitrate in acid solution.

> To chloroform (1 ml.) add bench sodium hydroxide solution (5 ml.) and boil the mixture *gently* until no more oily drops are visible. Cool the mixture, *acidify* it with dilute nitric acid, and add silver nitrate solution; a white precipitate of silver chloride, " soluble " in ammonium hydroxide solution, is formed.

14, 25   **FORMALDEHYDE**

Formaldehyde ($H.CHO$ or H_2CO) is a gas (b.p. −21°). It undergoes most of the general reactions of aldehydes (condensation reactions, see pp. 330–332; reductions, see pp. 333–334) and has certain special chemical properties of its own.

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[1] It is also used as a preservative to prevent bacterial decomposition of urine samples.

used for fixing histological specimens and for sterilising surgical instruments. Gaseous formaldehyde, obtained by heating paraformaldehyde, is used for disinfecting rooms after cases of infectious sickness.

REACTIONS

1. Polymerisation on Heating.

(*Fume Cupboard.*) Evaporate formalin (2 ml.) to dryness in a porcelain basin over the boiling water bath. A white solid, paraformaldehyde, remains. Keep this for comparison with the product obtained in reaction 2.

2. Reaction with Ammonia.

Formaldehyde on heating with ammonia yields hexamethylene tetramine (hexamine or urotropine, $(CH_2)_6N_4$), a white solid used as a urinary antiseptic.

(*Fume Cupboard.*) Mix formalin (1 ml.) and concentrated ammonia solution (1 ml.) and evaporate to dryness on the boiling water bath. A white solid, hexamine, remains. Show by the sodium-fusion test that this contains nitrogen, whereas the product obtained in reaction 1 does not.

Hexamine on heating with dilute mineral acids is hydrolysed, yielding formaldehyde and an ammonium salt.

Boil hexamine (1 spatula-point) with dilute sulphuric acid for a minute. Formaldehyde is evolved (smell). Basify with dilute sodium hydroxide—ammonia is liberated (smell).

3. Reaction with Sodium Hydroxide.

On heating with dilute sodium hydroxide formaldehyde undergoes the Cannizzaro reaction (see p. 335) and no visible change takes place. With more concentrated sodium hydroxide, a yellow polymeride is produced (compare other aliphatic aldehydes, p. 335).

(*a*) Boil together formalin (2 ml.) and bench sodium hydroxide solution (2M, 2 ml.). No visible change occurs.

(*b*) Boil together formalin (0.5 ml.) and sodium hydroxide solution (5M, 2 ml.). A yellow colour is produced.

14, 26   CHLORAL HYDRATE

Chloral hydrate, $CCl_3CH(OH)_2$, ... mpound in which two hyc . . . . rbon atom (hydrated carbo . . . . . . soluble in water, alcohol or ether.

Its chemical properties are chiefly those expected of a polyhalogen compound and a hydrated aldehyde.

It is used in medicine as a hypnotic.

REACTIONS

1. Reducing Properties.

Chloral hydrate reduces Fehling's Solution on heating, and ammoniacal silver nitrate solution in the cold. Carry out these tests as for carbonyl compounds (see pp. 333-334).

2. Behaviour with Alkali.

Sodium hydroxide hydrolyses the C—C bond in chloral hydrate, yielding chloroform and sodium formate. A similar reaction has already been met as part of the iodoform test (see p. 335).

$$CCl_3.CH(OH)_2 + OH^- \ \rightleftharpoons \ HCCl_3 + HCOO^- + H_2O.$$

To chloral hydrate (1 spatula-point) add bench sodium hydroxide solution (2 ml.) and shake. The solution becomes cloudy owing to the separation of chloroform (smell).

14, 27   **FORMIC ACID**

The molecule of formic acid H—C $\diagup^{\textstyle O}_{\diagdown O-H}$ contains, in addition to

the carbonyl radical (COOH), the aldehyde radical (CHO). While it undergoes the usual reaction of carboxylic acids (salt-formation, ṣṭ̣ẹṛ̣ịf̣ịc̣ạṭịọṇ, ẹṭc̣.) ịṭ ạṇḍ ịṭṣ ṣạḷṭṣ ạḷṣọ p̣ọṣṣẹṣṣ some of the properties · ẹṣ · . ' · acid acts as a reducing

$$H.COOH + (O) = CO_2 + H_2O$$
or $$H.COOH - 2e = CO_2 + 2H^+.$$

A further special reaction (dehydration) is noted below. All common metallic formates are soluble in water.

Formic acid is of no medical importance.

REACTIONS

1. Reducing Properties.

(a) Reduction of Ammoniacal Silver Nitrate.

Formates reduce ammoniacal silver nitrate to metallic silver (black precipitate, *not* mirror).

To ammoniacal silver nitrate solution (2 ml.) add sodium formate solution (2 ml.) and warm. Silver is produced as a black precipitate.

(b) *Reduction of Permanganate.*

Formic acid or formates reduce permanganate in warm acid solution to manganous salt.

To sodium formate solution (2 ml.) add bench dilute sulphuric acid (5 ml.), warm gently and add potassium permanganate solution (0·1%, 5 drops). The latter is decolorised immediately.

(c) *Reduction of a Mercuric Salt.*

Formic acid or formates reduce mercuric salts to mercurous salts. If mercuric chloride is used, a white precipitate of mercurous chloride is formed.

$$2Hg^{++} + HCOO^- = Hg_2^{++} + H^+ + CO_2.$$
$$Hg_2^{++} + 2Cl^- = Hg_2Cl_2\downarrow.$$
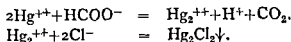
To sodium formate solution (2 ml.) add mercuric chloride solution (2 ml.) and warm. A white precipitate of mercurous chloride is formed. This is turned grey by ammonia.

2. Dehydration.

Formic acid on heating with concentrated sulphuric acid is dehydrated to carbon monoxide (CO), which on ignition burns vigorously with a pale-blue flame.

$$H.COOH = CO + H_2O \text{ (dehydration).}$$
$$2CO + O_2 = 2CO_2 \text{ (burning).}$$
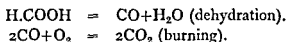
Formates are converted by concentrated sulphuric acid to formic acid, which is then dehydrated as above.

To formic acid (1 ml.) add concentrated sulphuric acid (1 ml.) and heat. Ignite the evolved gas but do *not* inhale it.

14, 28   OXALIC ACID

Oxalic acid $(COOH)_2$, the simplest dicarboxylic acid, is usually met as the dihydrate $(COOH)_2, 2H_2O$. This is a crystalline solid (solubility in water at 20°, 10 g. per 100 ml.). The pK values of the acid are—first dissociation $pK_a = 1.24$; second dissociation $pK_a = 4.21$. Note that, as far as the first stage of dissociation is concerned, the acid is considerably stronger than acetic acid.

The acid undergoes the usual reactions of acids (*e.g.*, salt formation and esterification)

to blood removes calcium ions. Since the latter are necessary for the clotting of blood, blood to which oxalate has been added does *not* clot.

REACTIONS

1. Reducing Properties.

Chloral hydrate reduces Fehling's Solution on heating, and ammoniacal silver nitrate solution in the cold. Carry out these tests as for carbonyl compounds (see pp. 333-334).

2. Behaviour with Alkali.

Sodium hydroxide hydrolyses the C–C bond in chloral hydrate, yielding chloroform and sodium formate. A similar reaction has already been met as part of the iodoform test (see p. 335).

$$CCl_3.CH(OH)_2 + OH^- = HCCl_3 + HCOO^- + H_2O.$$

To chloral hydrate (1 spatula-point) add bench sodium hydroxide solution (2 ml.) and shake. The solution becomes cloudy owing to the separation of chloroform (smell).

FORMIC ACID

The molecule of formic acid $H-C\!\!\begin{array}{c} \nearrow O \\ \searrow O-H \end{array}$ contains, in addition to

the carbonyl radical (COOH), the aldehyde radical (CHO). While it undergoes the usual reaction of carboxylic acids (salt-formation, esterification, etc.), it and its salts also possess some of the properties of aldehydes (reducing properties). When the acid acts as a reducing agent it is oxidised to carbon dioxide and water.
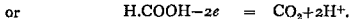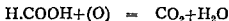
$$H.COOH + (O) = CO_2 + H_2O$$

or $$H.COOH - 2e = CO_2 + 2H^+.$$

A further special reaction (dehydration) is noted below. All common metallic formates are soluble in water.

Formic acid is of no medical importance.

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1. Reducing Properties.

(a) Reduction of Ammoniacal Silver Nitrate.

Formates reduce ammoniacal silver nitrate to metallic silver (black precipitate, *not* mirror).

To ammoniacal silver nitrate solution (2 ml.) add sodium formate solution (2 ml.) and warm. Silver is produced as a black precipitate.

14, 29

ALIPHATIC HYDROXY-ACIDS

Three aliphatic hydroxy-acids are considered here, two of which are of great biological importance, viz. :

Lactic Acid (α-hydroxypropionic acid, $CH_3.CHOH.COOH$). This is a normal intermediate in carbohydrate metabolism in muscle. It is also a product of bacterial fermentation in certain pathological conditions of the stomach, and in milk which has become sour. It is a constituent of the " organic acid " fraction estimated in the analysis of gastric contents after a test meal.

Citric Acid

$$\begin{array}{c} \text{OH} \\ | \\ \text{COOH.CH}_2.\text{C.CH}_2.\text{COOH} \\ | \\ \text{COOH} \end{array}$$

This may be concerned in carbohydrate metabolism in the animal body ; it is present in the juice of citrus fruits.

Tartaric Acid (dihydroxysuccinic acid, $COOH.CHOH.CHOH.$ $COOH$). This acid is included chiefly on account of its chemical interest. It is found in many fruits (especially the grape). Its potassium antimonyl salt is used as an emetic (tartar emetic).

The acids undergo the ....

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acids are readily soluble in water, and all are *weak* acids, pK_a values being as follows :

Lactic acid	3·86
Citric acid (first stage)	3·10
,, (second stage)	4·75
,, (third stage)	6·41
Tartaric acid (first stage)	3·01
,, (second stage)	4·39

The sodium, potassium and ammonium salts of all the acids are soluble in water. Regarding the solubilities of the other salts, only the following need be noted : Calcium lactate is soluble in water ; calcium tartrate is insoluble in water. Calcium citrate is slightly soluble in cold water (less in hot) ; its solution does *not* contain calcium ions.

Citrate (which is *non-toxic*) is added to blood when it is taken from donors for transfusions, to transform calcium into an unionised form and so to prevent clotting (compare oxalate, p. 420). Citrate is also used for the same purpose in certain clinical tests, *e.g.*, in determination of the blood sedimentation rate.

Milk to which ....   lcium ions.
It   · digested ;
it   : is desired
to provide a diet which can easily be digested.

Samples of blood for examination are therefore often treated with oxalate immediately after withdrawal, to prevent clotting.

Calcium ions are also necessary for the clotting of milk by rennin, an enzyme secreted by the gastric mucosa. Oxalate-treated milk is therefore not clotted by rennin.

Oxalic acid and oxalates are *poisonous* and cannot therefore be used as anti-coagulants for blood to be used in transfusions or for the preparation of invalid milk (contrast citrates, p. 421). Oxalates occur in small quantities in many vegetables and in larger quantities in rhubarb leaves (hence the poisonous character of the latter). Oxalates are present in normal urine in small quantity ; in certain pathological conditions the amount is greatly increased and calcium oxalate may crystallise out as "urinary stones" in the bladder or appear as a deposit in urine on standing.

REACTIONS

1. Ionic Reactions.

Calcium oxalate is insoluble in water and in dilute acetic acid, but "soluble" in dilute hydrochloric acid. Ferric oxalate is soluble in water and is not deeply coloured (contrast acetate, p. 339, and lactate, p. 422).

> To oxalic acid (1 spatula-point) in water (1 ml.) add calcium chloride solution (5 drops). A white precipitate of calcium oxalate is formed. Test its solubilities in dilute acetic acid and dilute hydrochloric acid.

2. Dehydration.

Oxalic acid or oxalates on heating with concentrated sulphuric acid yield a mixture of carbon dioxide and carbon monoxide. The reaction is a dehydration : $H_2C_2O_4 = CO + CO_2 + H_2O$. On ignition, the carbon monoxide burns with a blue flame, although not as vigorously as the pure carbon monoxide obtained in the same conditions from formic acid.

> Heat oxalic acid (2 spatula-points) with concentrated sulphuric acid (1 ml.). Ignite the gases evolved.

3. Oxidation.

Oxalic acid is quantitatively oxidised by warm acid permanganate to carbon dioxide and water.

$$H_2C_2O_4 + (O) = 2CO_2 + H_2O,$$
$$\text{or} \qquad H_2C_2O_4 - 2e = 2CO_2 + 2H^+.$$

This reaction is used in volumetric analysis (see pp. 154–155).

> Dissolve oxalic acid (1 spatula-point) in dilute sulphuric acid (2 ml.) with heating. Add potassium permanganate solution (5 drops). The colour of the permanganate is discharged.

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The acids undergo the general reactions of the carboxyl and hydroxyl radicals. Special reactions of interest are described below.

Lactic acid is a liquid, the other two acids are solids. All three acids are readily soluble in water, and all are *weak* acids, pK_a values being as follows :

Lactic acid	.	.	.	.	3·86
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The sodium, potassium and ammonium salts of all the acids are soluble in water. Regarding the solubilities of the other salts, only the following need be noted : Calcium lactate is soluble in water ; calcium tartrate is insoluble in water. Calcium citrate is slightly soluble in cold water (less in hot) ; its solution does *not* contain calcium ions.

Citrate (which is *non-toxic*) is added to blood when it is taken from donors for transfusions, to transform calcium into an unionised form and so to prevent clotting (compare oxalate, p. 420). Citrate is also used for the same purpose in certain clinical tests, *e.g.*, in determination of the blood sedimentation rate.

Milk, to which citrate has been added, contains no free calcium ions. It is not clotted by rennin in the stomach and is more easily digested ; it is therefore administered in certain conditions where it is desired to provide a diet which can easily be digested.

REACTIONS

1. Colours with Ferric Chloride.

Aliphatic α-hydroxy-acids (*e.g.*, lactic, tartaric and citric acids) give *yellow* colours with ferric chloride. These colours are due to the formation of complex ions. The colours are *not* produced in the presence of strong mineral acid ; if a solution containing such an acid (*e.g.*, gastric juice) is to be tested for α-hydroxy-acid, the latter must be removed by extraction with ether and the ether evaporated before the ferric chloride test is used (see (*b*)). A modification of the ferric chloride test used in biological work (Uffelmann's test) involves the displacement of phenol from its purple ferric iron complex by the hydroxyacid (see (*c*)).

(*a*) Carry out the following test with a 0·1% aqueous solution of each of the three acids, and with water as a negative control. To a solution of the acid (or water) (5 ml.) add bench ferric chloride solution (2 drops). Compare the yellow colours produced by the acids with the negative control. Then add dilute hydrochloric acid (1 ml.) to each of the tubes containing the hydroxy-acids—the colours are discharged.

(*b*) Take 10 ml. of the given solution containing lactic acid and hydrochloric acid. Test 5 ml. of this sample immediately with ferric chloride as above in (*a*).

Shake the other 5 ml. of the original sample with ether (5 ml.) in a test-tube. Pipette the upper (ether) layer into another test-tube and evaporate the ether by warming in a previously warmed water-bath (*keep away from all flames*). The residue is lactic acid, now free from hydrochloric acid. Dissolve this residue in water (5 ml.) and test with ferric chloride as before. Compare the colours obtained with this solution and with the untreated mixture.

(*c*) *Uffelmann's Test.*

Dissolve phenol (¼ spatula-point) in water (2 ml.) and add *ferric chloride solution (1 drop). A purple colour is produced.* Add lactic acid (1 drop). The colour changes to yellow.

2. Behaviour with Hot Concentrated Sulphuric Acid.

All the acids char. Lactic acid gives off carbon monoxide, tartaric and citric acids give off a mixture of carbon monoxide and carbon dioxide.

Heat the acid (1 spatula-point of solid acids ; 10 drops lactic acid) with concentrated sulphuric acid (1 ml.). Try to ignite the evolved gases.

3. Iodoform Test (Lactic Acid).

Lactic acid gives the iodoform test since it contains the grouping $CH_3.CHOH$. Carry out the test as for ethyl alcohol (see p. 335).

4. Reduction of Ammoniacal Silver Nitrate (Tartrates).

Tartrates reduce ammoniacal silver nitrate solution on warming, giving a silver mirror. This may be due to the production of an aldehyde by tautomerism.
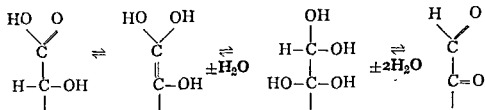
Carry out the test as for aldehydes (see p. 333).

5. Formation of Fehling's Solution (Tartrates).

Tartrates or tartaric acid dissolve copper hydroxide, giving a deep blue solution, containing a complex copper-tartrate ion. The solution so obtained is Fehling's Solution, used in testing for aldehydes and for reducing sugars.

To copper sulphate solution (2 ml.) add sodium hydroxide solution (2 ml.). A pale-blue precipitate of copper hydroxide is formed. Dissolve tartaric acid (1 spatula-point) in water (2 ml.) and add the solution to the copper hydroxide. The latter is dissolved, giving a clear deep-blue solution.

14, 30 ACETOACETIC ACID AND RELATED COMPOUNDS

Acetoacetic acid (β-ketobutyric acid, $CH_3.CO.CH_2.COOH$) its decarboxylation product acetone
hydroxy-acid (β-hydroxybutyr
known collectively as the "acetone bodies"—are present in human urine—in small quantities normally, in much larger quantities in cases of diabetes mellitus and starvation. The physical properties of the acids need not be considered here. Two reactions are detailed below. One, the nitroprusside test, given by acetoacetic acid and by acetone, is a general reaction of compounds containing the grouping $CH_3.CO$ (see p. 334) modified as not to

alone; it is due to complex ion formation (compare α-hydroxy-acids). Other substances (e.g., phenolic compounds) which give similar colours may be present in urine after the administration of drugs, e.g., aspirin, and may cause confusion.

REACTIONS

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Shake the other 5 ml. of the original sample with ether (5 ml.) in a test-tube. Pipette the upper (ether) layer into another test-tube and evaporate the ether by warming in a previously warmed water-bath (*keep away from all flames*). The residue is lactic acid, now free from hydrochloric acid. Dissolve this residue in water (5 ml.) and test with ferric chloride as before. Compare the colours obtained with this solution and with the untreated mixture.

(*c*) *Uffelmann's Test.*

Dissolve phenol (¼ spatula-point) in water (2 ml.) and add ferric chloride solution (1 drop). A purple colour is produced. Add lactic acid (1 drop). The colour changes to yellow.

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3. Iodoform Test (Lactic Acid).

Lactic acid gives the iodoform test since it contains the grouping $CH_3.CHOH$. Carry out the test as for ethyl alcohol (see p. 335).

determination of urea the ammonium carbonate formed is decomposed by caustic alkali, and the ammonia driven over into a known amount of standard acid, the excess of which can then be determined by titration.

2. Reaction with Nitrous Acid.

Urea reacts with nitrous acid to give nitrogen and carbonic acid, which then gives carbon dioxide and water.

$$CO(NH_2)_2 + 2O:N.OH = CO_2 + 2N_2 + 3H_2O.$$
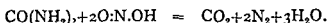
Dissolve urea (1 spatula-point) in water (2 ml.). Add a solution of nitrous acid (2 ml.) prepared as for reaction with acetamide. Carbon dioxide and nitrogen are evolved.

3. Salt Formation.

Urea acts as a monoacidic base. Some salts which are sparingly soluble in water—*e.g.*, the nitrate $CO(NH_2)_2.HNO_3$ and the oxalate $2CO(NH_2)_2.(COOH)_2$—serve for its identification.

Make a solution of urea (4 spatula-points) in water (2 ml.). Mix this solution (1 ml.) with concentrated nitric acid (1 ml.). A precipitate of urea nitrate is formed. Repeat, using saturated oxalic acid instead of nitric acid. Urea oxalate is formed.

4. Reaction with Hypobromite.

Urea is oxidised by hypobromites, giving nitrogen and carbon dioxide.

$$CO(NH_2)_2 + 3OBr^- = 3Br^- + 2H_2O + CO_2 + N_2.$$
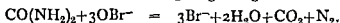
If sufficient sodium hydroxide is added to the hypobromite all carbon dioxide is absorbed. Determination of the volume of the nitrogen remaining forms the basis of the " ureometer " method for the determination of urea in urine.

Dissolve urea (1 spatula-point) in water (2 ml.) and add sodium hypobromite solution (2 ml.). A vigorous effervescence occurs.

5. Biuret Reaction.

Urea on heating alone yields ammonia, biuret and other products. Biuret ($NH_2.CO.NH.CO.NH_2$) gives with copper sulphate and alkali a purple colour (compare proteins, p. 402).

wh
dis
(3 ml.) and add copper sulphate solution (1 drop). A purple colour is produced. (Excess copper sulphate gives a blue precipitate which masks the purple colour.)

REACTIONS

1. **Colour with Nitroprusside (Rothera's Test).**

Saturate an aqueous solution of acetone (0·1%, 5 ml.) with ammonium sulphate, *i.e.*, add the solid until some remains undissolved. Add freshly-prepared sodium nitroprusside solution (5%, 2 drops) and run on to the surface of the solution concentrated aqueous ammonia (3 ml.). A purple colour develops slowly at the interface between the two liquid layers.

2. **Colour with Ferric Chloride (Gerhardt's Test).**

To a solution of acetoacetic acid (0·1%, 2 ml.) add ferric chloride solution (1 drop). A deep-red colour is produced.

14, 31   UREA

Urea (carbamide $CO.(NH_2)_2$) is a white crystalline solid (m.p. 132°), readily soluble in water and alcohol. In some reactions (*e.g.*, with alkali and nitrous acid) urea resembles the simple amides (see pp. 350-351); in others it shows peculiar properties (*e.g.*, it acts as a monacidic base). It is probable that urea exists in two or more tautomeric forms:

$$
O=C\begin{array}{c} NH_2 \\ \\ NH_2 \end{array}
\;\rightleftharpoons\;
HO-C\begin{array}{c} NH \\ \\ NH_2 \end{array}
\;\rightleftharpoons\;
{}^-O-C\begin{array}{c} NH_2{}^+ \\ \\ NH_2 \end{array}
$$
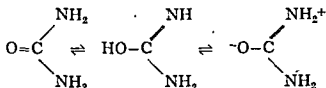
quantities of many other constituents (some important).

REACTIONS

1. **Hydrolysis.**

Urea is hydrolysed very slowly by alkali, giving ammonia.

$$CO(NH_2)_2 + 2OH^- = CO_3^{--} + 2NH_3\uparrow.$$

Boil urea (1 spatula-point) with sodium hydroxide solution (3 ml.). Note the smell of ammonia (evolved *very* slowly).

Urea is also hydrolysed by the enzyme urease thus:

$$CO(NH_2)_2 + 2H_2O = CO_3^{--} + 2NH_4^+.$$
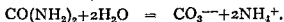
This reaction is used in the detection and determination of urea. Ammonium carbonate is hydrolysed in solution and reacts alkaline, since ammonium hydroxide is stronger than carbonic acid. A solution containing urea therefore becomes alkaline as urease acts on it. In the

14, 33   **PURINES**

The purine skeleton III or IV [1] is used by nature for a wide variety

III   IV

of purposes. It is present in constituents of nucleic acids (adenine and guanine), in certain alkaloids (caffeine) and in uric acid, an important minor constituent of urine.

Uric acid (2:6:8-trihydroxypurine, $C_5H_4N_4O_3$) exists in two tautomeric modifications known as "lactam" and "lactim" forms.

Lactam form   Lactim form

This acid will be used as a representative of the purine group in the laboratory.

The acid is a white solid, very sparingly soluble in water ($s = 0.006$ g. per 100 ml.); one hydroxyl group of the lactim form ionises very slightly ($pK_a = 5$). The alkali urates are more soluble in water than uric acid, which therefore "dissolves" in dilute alkalis and alkali carbonates.

Reactions

1. Murexide Test.

This test depends on the oxidative destruction by nitric acid of the five-membered rings in two purine molecules and the combination of the two remaining pyrimidine nuclei.

(2 ~~Dissolve uric~~ ...
(2 ~~drops~~ in a ~~basin~~. Evaporate the mixture to dryness over a very small flame, taking care not to char it. Add to the residue ammonium hydroxide solution (1 drop); a violet colour is produced.

[1] The skeleton is usually written in the form III, which shows the relationship of the purines to urea, two N.C.N. units being clearly displayed. Form IV gives a more correct picture of the relative positions of the atoms in space.

The cyclic ureides of many substituted malonic acids (barbituric acids) are used in medicine as anaesthetics or hypnotics. The general formula of these compounds is I (below).
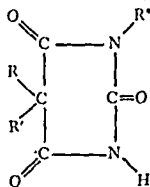
Barbituric Acids

I
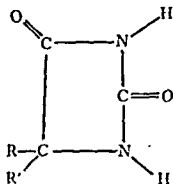
Hydantoins

II

In the barbituric acids used in medicine R and R' are always hydro-carbon radicals, R" may be hydrogen or a hydrocarbon radical.

All these compounds are weak acids due to the presence of one or two hydrogen atoms in imide radicals .CO.NH.CO (compare uric acid, p. 428). The free acids are hardly ionised at all and are mostly sparingly soluble in water; they are therefore useless for parenteral administration. Their sodium salts, however, are ionised and are soluble in water; they can therefore be used for injection (compare behaviour of uric acid or of benzoic acid). This is an excellent example of the practical importance of ionised links in conferring water-solubility on a compound.

Compounds of a somewhat similar structure, but with a five-membered ring (hydantoin derivatives) (formula II above), are also used as depressants of the central nervous system.

REACTIONS

Barbitone (diethylbarbituric acid) is used to illustrate the reactions of this class of compound.

Solubility and Acidic Nature.

(a) To barbitone (2 spatula-points) in an ignition-tube add water (5 drops). The substance does not dissolve in the cold, but dissolves on boiling and recrystallises on cooling.

(b) To barbitone (½ spatula-point) in an ignition-tube add dilute sodium hydroxide (2 drops). The substance dissolves in the cold due to the formation of a sodium salt. Add dilute hydrochloric acid (2 drops); the free acid is reprecipitated.

14, 33

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REACTIONS

1. Murexide Test.

This test depends on the oxidative destruction by nitric acid of the five-membered rings in two purine molecules and the combination of the two remaining pyrimidine nuclei.

Dissolve uric acid ($\frac{1}{10}$ spatula-point) in sodium carbonate solution (2 ml.). Mix this solution (2 drops) with concentrated nitric acid (2 drops) in a basin. Evaporate the mixture to dryness over a very small flame, taking care not to char it. Add to the residue ammonium hydroxide solution (1 drop); a violet colour is produced.

[1] The skeleton is usually written in the form III, which shows the relationship of the purines to urea, two N.C.N. units being clearly displayed. Form IV gives a more correct picture of the relative positions of the atoms in space.

2. Solubility in Water and Alkali.

Examine the solubility of uric acid in water and in sodium carbonate solution as follows :

(a) To uric acid ($\frac{1}{16}$ spatula-point) add water (3 ml.) and boil. The acid remains undissolved.

(b) To uric acid ($\frac{1}{16}$ spatula-point) add sodium carbonate solution (2 ml.) and boil. Some of the acid goes into solution as sodium urate. Cool and filter the solution and acidify the filtrate with concentrated hydrochloric acid. Uric acid is precipitated.

3. Reducing Properties.

(a) Fehling's Solution.

Uric acid reduces Fehling's Solution *slowly* (contrast glucose, p. 389). The difference in speed of reduction is important in clinical work since it makes possible a rough distinction between *diabetic* urines which contain uric acid plus *glucose* (and therefore reduce Fehling's Solution *rapidly*), and *normal* urines which contain uric acid but no glucose (and may therefore reduce Fehling's Solution *slowly*).

Boil uric acid ($\frac{1}{16}$ spatula-point) with sodium carbonate solution

(b) Folin's Reagent.

Uric acid reduces Folin's reagent, which is a solution of phosphotungstic acid, to a deep blue product. This reaction forms the basis of a colorimetric method for the determination of uric acid.

Dissolve uric acid ($\frac{1}{16}$ spatula-point) in sodium carbonate solution (2 ml.) and add to this Folin's reagent (2 drops). A deep blue colour is produced.

14, 34   CREATININE

Creatinine, the lactam or inner anhydride of creatine (methylguanidinoacetic acid), has the formula

It is a white solid, soluble in water, and is a normal constituent of urine.

REACTIONS

1. Colour with Nitroprusside (Weyl's Test).

Creatinine, like other compounds containing the grouping $CH_2.CO$, gives a red colour with nitroprusside in the presence of caustic alkali. (compare p. 334). It does not, however, give a colour with nitroprusside in the presence of ammonia (contrast acetone and acetoacetic acid, Rothera's test, p. 424).

(a) To an aqueous solution of creatinine (0·1%, 2 ml.) add sodium nitroprusside solution (5%, 2 drops). Then add sodium hydroxide solution (10 drops); a bright red colour is produced. Acidify with glacial acetic acid; the colour changes to a very pale yellow.

(b) Carry out Rothera's test, using a solution of creatinine (0·1%) instead of a solution of acetone.

2. Colour with Picric Acid (Jaffe's Test).

Creatinine gives with picric acid in alkaline solution a red colour due to the formation of a picrate. The reaction forms the basis of a colorimetric method for the determination of creatinine.

To an aqueous solution of creatinine (2 ml.) add a saturated aqueous solution of picric acid (2 drops) and bench sodium hydroxide solution (2 drops). The solution becomes deep orange. Carry out a negative control test with water.

14, 35   SULPHURIC ACID ESTERS

Organic hydroxy compounds (alcohols and phenols) can form esters with inorganic as well as organic acids, e.g., sulphates (potassium phenyl sulphate, $C_6H_5OSO_2OK$), phosphates (glycerophosphoric acid, $CH_2OH.CHOH.CH_2.O.PO_2(OH)_2$), nitrites (amyl nitrite, $C_5H_{11}.O.N:O$), nitrates ("nitroglycerin," glyceryl trinitrate, $CH_2O(NO_2).CHO(NO_2).CH_2O(NO_2)$).

In the sulphates of hydroxy compounds the alkyl or aryl radical is covalently linked to sulphur through oxygen; the compounds therefore do not give the reactions of the sulphate ion.

The esters are hydrolysed by heating with acid, thus, e.g.,

$$C_6H_5O.SO_2O^- + H^+ + HOH \;=\; C_6H_5OH + SO_4^{--} + 2H^+.$$

The resulting solution gives the reactions of the sulphate ion. Sulphonic acids $Ar.SO_2.OH$ are not hydrolysed in these conditions (see comparative experiment 2 (b) below).

Many undesirable hydroxy compounds, if produced in or introduced into the animal body, are detoxicated by the formation of sulphates, which are excreted in the urine. Examples are (i) indole (produced by the action of intestinal bacteria on tryptophane, and absorbed from the large intestine), which is excreted as indoxyl-sulphuric acid (indican), (ii) phenols (introduced into the body as antiseptics) which are excreted as their sulphates.

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The hydroxy compounds are said to be "conjugated" with sulphuric acid, and the esters are often described incorrectly as "ethereal sulphates."

1. Absence of Sulphate Ion.

To a solution of potassium phenyl sulphate (2 ml.) add barium nitrate solution (5 drops) and dilute nitric acid (5 drops). No precipitate is produced, therefore no sulphate ion is present.

2. Hydrolysis to Phenol and Sulphuric Acid.

(a) To a solution of potassium phenyl sulphate (2 ml.) add dilute hydrochloric acid (2 ml.) and boil for two minutes. Note the smell of phenol in the escaping steam. Cool and add barium nitrate solution (5 drops). A precipitate (barium sulphate) is produced.

(b) Repeat (a), using a solution of p-toluenesulphonic acid instead of potassium phenyl sulphate. No phenol is produced and no precipitate is formed on the addition of barium nitrate solution.

14, 36   SALICYLIC ACID AND ITS DERIVATIVES

Salicylic acid (o-hydroxybenzoic acid, $HO.C_6H_4.COOH$) and many of its derivatives are of medical importance, chiefly as antipyretics, analgesics and antiseptics. Formulæ, names and properties of some important compounds are as follows :

Formula	Chemical Name	Common Name	Properties	Uses
C_6H_4 $\langle$ OH COOH	Salicylic acid	—	Solid, m.p. 159°; weak acid (pK$_a$ = 2·98); s in water, 0.18 g. per 100 ml.*	(Acid and Na salt) treatment of rheumatism.
C_6H_4 $\langle$ OOCCH$_3$ COOH	Acetylsalicylic acid	Aspirin	Solid, m.p. 133°; s in water, 0·25 per 100 ml.*	Antipyretic Mild analgesic
C_6H_4 $\langle$ OH COOCH$_3$	Methyl salicylate	Oil of wintergreen	Liquid, b.p. 223°; s in water, 0·08 g. per 100 ml.	Counterirritant
C_6H_4 $\langle$ OH COOC$_6$H$_5$	Phenyl salicylate	Salol	Solid, m.p. 43°; s in water, 0 02 g. per 100 ml.	Intestinal antiseptic

* The sodium salts of salicylic acid and acetylsalicylic acid are readily soluble in water.

The most important reactions of these compounds are the general reactions of the substituent radicals present, viz. carboxyl, phenolic hydroxyl and ester.

REACTIONS OF THE ACID

1. Esterification.

Salicylic acid with methyl alcohol and a trace of concentrated sulphuric acid yields methyl salicylate. Carry out the reaction as for the preparation of ethyl benzoate (p. 323).

2. Decarboxylation.

Salicylic acid on heating with soda-lime yields phenol. Carry out the reaction as for benzoic acid (p. 340).

3. Ferric Chloride Reaction.

Salicylic acid and acetylsalicylic acid and their salts give purple colours with ferric chloride (compare phenols and see details of reaction, p. 325).

REACTIONS OF THE ESTERS

4. Hydrolysis.

The hydrolysis of the esters acetylsalicylic acid, methyl (or ethyl) salicylate and phenyl salicylate and the separation of the products by modification of the methods used for ethyl benzoate (see p. 342) provide useful additional experiments if required.[1]

14, 37   **ACETANILIDE**

Acetanilide (acetylaniline, N-phenylacetamide, $C_6H_5.NH.CO.CH_3$) is a white solid (m.p. 114°). It is sparingly soluble in water and is neutral; it is *not* more soluble in dilute acid or alkali than in water (contrast aniline). It can be hydrolysed by boiling with acids and (*very* slowly) by boiling with alkali (compare and contrast unsubstituted amides).

It is used in medicine as an antipyretic.

REACTIONS

1. Solubility.

Compare the solubilities of acetanilide in water, dilute hydrochloric acid and sodium hydroxide, employing the usual quantities (see pp. 312-313).

2. Hydrolysis.

(The apparatus is the same as for hydrolysis of ethyl benzoate, p. 342.)

Boil acetanilide (1 g.) and 70% sulphuric acid (10 ml.) under reflux for 20 minutes. The mixture smells of acetic acid. Add water (10 ml.) and distil about 5 ml. of liquid. Test this distillate for acetic acid. Cool the liquid which has not been distilled, and test this for aniline, which is present as its sulphate.

---

[1] Instructors should decide to what extent students can be expected to devise their own methods.

The hydroxy compounds are said to be "conjugated" with sulphuric acid, and the esters are often described incorrectly as "ethereal sulphates."

1. Absence of Sulphate Ion.

To a solution of potassium phenyl sulphate (2 ml.) add barium nitrate solution (5 drops) and dilute nitric acid (5 drops). No precipitate is produced, therefore no sulphate ion is present.

2. Hydrolysis to Phenol and Sulphuric Acid.

(a) To a solution of potassium phenyl sulphate (2 ml.) add dilute hydrochloric acid (2 ml.) and boil for two minutes. Note the smell of phenol in the escaping steam. Cool and add barium nitrate solution (5 drops). A precipitate (barium sulphate) is produced.

(b) Repeat (a), using a solution of p-toluenesulphonic acid instead of potassium phenyl sulphate. No phenol is produced and no precipitate is formed on the addition of barium nitrate solution.

14, 36   SALICYLIC ACID AND ITS DERIVATIVES

Salicylic acid (o-hydroxybenzoic acid, $HO.C_6H_4.COOH$) and many of its derivatives are of medical importance, chiefly as antipyretics, analgesics and antiseptics. Formulæ, names and properties of some important compounds are as follows :

Formula	Chemical Name	Common Name	Properties	Uses
C_6H_4 ⟨OH ⟨COOH	Salicylic acid	—	Solid, m.p. 159°; weak acid (pK_a= 2·98); s in water, 0.18 g. per 100 ml.*	(Acid and Na salt) treatment of rheumatism.
C_6H_4 ⟨OOCCH₃ ⟨COOH	Acetyl-salicylic acid	Aspirin	Solid, m.p. 133°; s in water, 0·25 per 100 ml.*	Antipyretic Mild analgesic
C_6H_4 ⟨OH ⟨COOCH₃	Methyl salicylate	Oil of winter-green	Liquid, b.p. 223°; s in water, 0 08 g. per 100 ml.	Counter-irritant
C_6H_4 ⟨OH ⟨COOC₆H₅	Phenyl salicylate	Salol	Solid, m.p. 43°; s in water, 0 02 g. per 100 ml.	Intestinal antiseptic

* The sodium salts of salicylic acid and acetylsalicylic acid are readily soluble in water.

2. Diazo Reaction.

This reaction consists of three stages, viz.:

(i) Diazotisation of the primary aromatic amino radical of the sulphonamide with nitrous acid; (ii) destruction of excess nitrous acid with ammonium sulphamate ($H_2N.SO_2.O-NH_4^+$); (iii) coupling of the diazo-compound with an aromatic amine (N-1-naphthylethylenediamine, $C_{10}H_7.NH.CH_2.CH_2.NH_2$), giving a purple colour (compare coupling with phenols, p. 348). This reaction is used in Bratton and Marshall's method for the determination of sulphonamides in blood or urine.

To a solution of sulphathiazole (10 mg. per litre, 10 drops) add dilute hydrochloric acid (2 drops), water (10 ml.) and sodium nitrite solution (0·1%, 1 ml.). Allow to stand 3 minutes and add ammonium sulphamate solution (0·5%, 1 ml.). Allow to stand 2 minutes and add N-1-naphthylethylenediamine hydrochloride solution (0·1%, 1 ml.). A purple colour slowly develops.

3. Formation of Schiff's Base.

The primary amino radical in sulphonamide drugs forms Schiff's base or anils with aromatic aldehydes (compare condensation of aniline and benzaldehyde, p. 347). The aldehyde used in determining sulphonamides is p-dimethylaminobenzaldehyde,[1] $(CH_3)_2N.C_6H_4.CHO$, which condenses to give an orange or red anil. The product obtained with sulphathiazole is $(CH_3)_2N.C_6H_4.CH:N.C_6H_4.SO_2.NH.C_3H_2NS$.

Dissolve sulphathiazole ($\frac{1}{10}$ spatula-point) in dilute hydrochloric acid (1 ml.), and add p-dimethylaminobenzaldehyde (solution in dilute sulphuric acid, 5 drops). An orange precipitate is produced. More dilute solutions of sulphonamides give orange or yellow colours.

14, 39   GLYCOSIDES

Glycosides are ethers formed by loss of water between the hydroxyl radical of the potential carbonyl grouping of a sugar (see p. 382) and some other hydroxy compound. They can be hydrolysed to the sugar and the non-sugar component (aglucone) by boiling dilute acids or by certain enzymes.

$$C_6H_{11}O_5\ OH^* + HO.C_6H_4.CH_2OH \rightleftharpoons C_6H_{11}O_5.OC_6H_4CH_2OH + HOH$$

glucose   salicyl alcohol   salicin
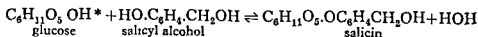
* This is the hydroxyl on the potential aldehyde group of glucose.

Glycosides are usually soluble in water or alcohol but insoluble in ether or benzene, owing to the high proportion of hydroxyl radicals in the sugar part of the molecule, even though the aglucone is virtually insoluble in water.

[1] This aldehyde is soluble in aqueous acids due to the presence of an amine radical.

14, 38   SULPHONAMIDE DRUGS

Derivatives of p-aminobenzenesulphonamide (sulphanilamide) are

$$H_2N - \langle benzene \rangle - SO_2 - NH_2$$
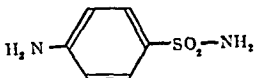
widely used as bacteriostatic agents, *i.e.*, in preventing the multiplication of bacteria. Most of these compounds have a substituent in place of one hydrogen atom of the sulphonamide radical, *e.g.*, in sulphathiazole a thiazole ring is substituted thus:

$$H_2N - \langle benzene \rangle - SO_2 - NH - \langle thiazole \rangle$$
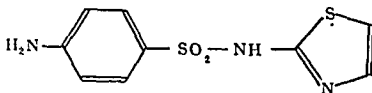
The important reactions of these compounds are those which would be expected from the substituent radicals they contain. The compounds are amphoteric, having weak basic properties due to the amino radical, and very weak acidic properties due to the sulphonamide radical. Although sparingly soluble in water they are more " soluble " in dilute acids and alkalis, due to salt formation by the amino and sulphonamide radicals respectively. The sodium salts of some sulphonamides (*e.g.*, p-NH$_2$.C$_6$H$_4$.SO$_2$N$^-$.C$_2$H$_2$NS, Na$^+$, sodium salt of sulphathiazole) are therefore used for parenteral administration.

The free sulphonamides are used for oral administration and for application to wounds.

Certain reactions, which are used to determine these drugs in blood and urine, depend on the presence of the primary aromatic amino radical. These are the diazo reaction (reaction 2) and the formation of a Schiff's base or anil (reaction 3).

REACTIONS

1. **Solubilities, Amphoteric Properties.**

(*a*) To sulphathiazole (1 spatula-point) add water (5 drops). The substance does not dissolve in the cold, but dissolves on warming and recrystallises on cooling.

(*b*) To sulphathiazole (1 spatula-point) add bench sodium hydroxide (1 drop). The substance dissolves immediately in the cold (formation of sodium salt). To the solution add 0·2M hydrochloric acid dropwise. A precipitate of free sulphathiazole forms and then redissolves (formation of hydrochloride of amino radical).

Different sterols give different colours in the Liebermann-Burchardt reaction described below. The mechanism of the reaction is unknown,

kofer reaction with sucrose and concentrated sulphuric acid is in principle the same as the Molisch test for carbohydrates, viz. formation of a coloured condensation-product between furfural (from sucrose) and a hydroxy compound (here cholic acid).

REACTIONS

1. Liebermann-Burchardt Reaction.

Take in a *dry* tube a solution of cholesterol in chloroform (2 ml.), add acetic anhydride (10 drops), shake, and after 1 minute add concentrated sulphuric acid (2 drops). The solution becomes red, then purple, blue and finally green.

2. Pettenkofer Reaction.

Mix in an ignition-tube sodium glycocholate solution (10 drops) and sucrose solution (10 drops). In another ignition-tube take concentrated sulphuric acid (1 ml.). Layer the glycocholate-sucrose solution on to this with a pipette. A purple ring is formed at the interface.

14, 41 ALKALOIDS

Alkaloids are complex nitrogenous bases of plant origin, many of which have valuable or dangerous pharmacological actions. They are of many different chemical types, but their most important properties are those of *amines of high molecular weight*. The free bases are sparingly soluble in water but readily soluble in organic solvents such as ether. The salts (*e.g.*, hydrochlorides or sulphates) are often readily soluble in water. The alkaloids can therefore be " dissolved " by hydrochloric or sulphuric acid, and then reprecipitated from these solutions by addition of alkali, and extracted with ether. Solutions of the salts give precipitates of insoluble salts with solutions containing various complex anions (*e.g.*, picrate, mercuri-iodide). Many alkaloids also give specific colour reactions, which are not conside . . .

a c

base. Quinine is much used in the treatment of malaria. A few other important alkaloids are morphine, strychnine, cocaine, atropine, nicotine.

REACTIONS

Use a 0·1% aqueous solution of quinine hydrochloride for these reactions.

1. Solubilities.

To quinine hydrochloride solution (5 ml.) add dilute sodium hydroxide (10 drops). A white precipitate of the free base,

Glycosides undergo some carbohydrate reactions (e.g., Molisch re-action and reaction with concentrated sulphuric acid), but not those reactions which depend on the presence of a free potential carbonyl group (e.g., reduction of Fehling's Solution).

Many glycosides are used as drugs. Digitalis or strophanthus preparations (powdered leaf or tinctures) containing steroid glycosides are used in the treatment of various cardiac conditions. Glycosides of polyhydroxyanthraquinones form the active principles of cascara, senna and similar preparations which are used as purgatives (anthracene purgatives).

Many water-soluble plant colouring-matters are glycosides, the two most important groups being the anthocyanins (red, purple and blue colours of flowers) and the anthoxanthins (yellow colours found in many parts of plants).

REACTIONS

1. Molisch's Test.

Carry this out as for glucose (p. 392), using a 0·5% solution of salicin.

2. Colour with Sulphuric Acid.

Many glucosides give red or purple colours with concentrated sulphuric acid, while carbohydrates give yellow, brown or black colours.

To salicin ($\frac{1}{8}$ spatula-point) add concentrated sulphuric acid (1 ml.). A red colour is produced in the cold.

3. Fehling's Test.

Glycosides do not reduce Fehling's Solution since the potential aldehyde radical of the sugar is not free. After hydrolysis of the glycoside, however, the free sugar shows reducing properties.

Test salicin with Fehling's Solution before and after hydrolysis as sucrose (p. 393).

14, 40   STEROIDS

The reduced cyclopentenophenanthrene or *steroid* skeleton is found
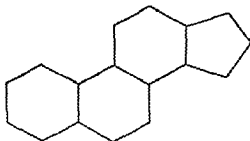
in many biologically-important compounds of widely differing func-tions (bile acids, sterols, male and female sex hormones, hormones of the adrenal cortex, cardiac glycosides, vitamin D).

Sterols form part of the "unsaponifiable fraction" of natural fats and oils. Cholesterol is a monohydroxy compound, $C_{27}H_{45}.OH$.

Applications of Chemistry to Clinical Medicine

Hawk, P. B., and Bergeim, O. Practical Physiological Chemistry, 11th edition. Churchill, London, 1938.

Harrison, G. A. Chemical Methods in Clinical Medicine, 2nd edition. Churchill, London, 1937.

Stewart, C. P., and Dunlop, D. M. Clinical Chemistry in Practical Medicine, 2nd edition. Livingstone, Edinburgh, 1937.

Peters, J. P., and Van Slyke, D. D. Quantitative Clinical Chemistry. 2 vols. Baillière, Tindall and Cox, London, 1932.

Bodansky, M., and Bodansky, O. Biochemistry of Disease. Macmillan, New York, 1940.

Mattice, M. R. Chemical Procedures for Clinical Laboratories. Kimpton, London, 1936.

Standing Committee on Laboratory Methods, University of Glasgow. Notes on Clinical Laboratory Methods, 5th edition. Smith, Glasgow, 1944.

quinine, is produced. Divide the mixture into two equal parts. Acidify one part with dilute hydrochloric acid; the quinine "dissolves" as its water-soluble hydrochloride is re-formed. Shake the other part of the alkaline mixture with ether (2 ml.); the quinine dissolves in this.

2. Precipitation of Insoluble Salts.

(a) *Picrate.* To quinine hydrochloride solution (2 ml.) add picric acid solution (5 drops). A yellow precipitate of quinine picrate is formed.

(b) *Mercuri-iodide.* Repeat (a), using potassium mercuri-iodide solution (Mayer's reagent), instead of picric acid. A white precipitate is formed.

FURTHER READING

PURE CHEMISTRY OF BIOLOGICALLY-IMPORTANT COMPOUNDS

Several of the books listed on pp. 307-308, notably those by READ (Text-Book), SCHMIDT, KARRER and GILMAN, deal with this to some extent.

JENKINS, G. L., and HARTUNG, W. H. The Chemistry of Organic Medicinal Products. Swift, St. Louis, 1941.

(Valuable for the chemistry of compounds used in medicine.)

ELEMENTARY THEORETICAL TEXT-BOOKS

PARSONS, T. R. Fundamentals of Biochemistry, 6th edition. Heffer, Cambridge, 1939.

THORPE, W. V. Biochemistry for Medical Students, 3rd edition. Churchill, London, 1943.

HARROW, B. Textbook of Biochemistry, 3rd edition. Saunders, Philadelphia, 1943.

BODANSKY, M. Introduction to Physiological Chemistry, 4th edition. Wiley, New York, 1938.

ELEMENTARY PRACTICAL TEXT-BOOKS

COLE, S. W. Practical Physiological Chemistry, 9th edition. Heffer, Cambridge, 1933.

PLIMMER, R. H. A. Organic and Bio-Chemistry, 6th edition. Longmans, Green, London, 1938.

IMPERIAL SYSTEM

The Imperial Units are those used in everyday life in Great Britain. The following table gives the relations between some metric and imperial units ; it includes approximate conversion factors which can be memorised, and factors to four significant figures, which can be used for more accurate work. The unit of time (the second) is the same in both systems.

	Imperial Sub-Unit	Approximate Factor	Accurate Factor
Mass .	Ounce avoirdupois (oz. av.)=437·5 grains Grain (gr.)	1 oz. av.=30 g. 1 gr.=60 mg.	1 oz. av.=28·35 g 1 gr.=64·80 mg.
Length .	Inch (in.)	1 in.=2·5 cm.	1 in.=2·540 cm.
Volume .	Fluid ounce (fl. oz.)=8 fl. dr. Fluid drachm (fl. dr.)=60 min. Minim (min.)	1 fl. oz.=30 ml. 1 fl. dr.=4 ml. 1 min.=0·06 ml.	1 fl. oz.=28·41 ml. 1 fl. dr.=3·551 ml. 1 min.=0·05919 ml.

APOTHECARIES' SYSTEM

This system is commonly used for the prescription of solids, the units of mass being as follows :

1 grain (gr.), *identical* with the Imperial grain.
1 drachm (℥)=60 gr.
1 ounce (℥)=480 gr. (*contrast* oz. av.).

SYMBOLS FOR PHYSICO-CHEMICAL QUANTITIES

These are all in general use and are taken chiefly from the recommendations of the Chemical Society.

d . . . density (g. per ml.).
s . . . solubility (*in this book*—in g. per 100 ml.).
K . . . chemical equilibrium constant (products/reactants).
K_s . . . solubility product.
e . . . (in equations) a Faraday or "gram-equivalent" of *electrons* (96,500 coulombs).
pH . . . $-\log$ [H^+]. The negative logarithm * of the
pK_a, pK_b . . . . ive logarithm of the
. . . . id or base.
b.p. . . . boiling-point (at 760 mm. pressure unless otherwise stated).
f.p. . . . freezing-point.
m.p. . . . melting-point.

* All logarithms in this book are to base 10.

OTHER SYMBOLS AND ABBREVIATIONS

Many of these are commonly but not universally employed, others may be peculiar to this book. *In all cases where doubt might arise, students should explain the meaning of the abbreviations they use.*

[X]	. .	*(thick* square brackets). Concentration of X in gram-molecules per litre or gram-ions per litre.
[ ]	. .	*(thin* square brackets) enclose the constituents of a complex ion.
↓	. .	precipitated.
↑	. .	evolved as gas.
→	. .	(in formulae) dative covalent link.
∞	. .	(solubility) miscible in all proportions.
HA	. .	any acid.
BOH	. .	any base.
BA	. .	any salt.
R	. .	any alkyl or aryl radical.
Alk	. .	any alkyl radical.
Ar	. .	any aryl radical.
Hal	. .	a halogen (Cl, Br, I).
conc.	. .	concentrated, concentration.
dil.	. .	dilute.
n	. .	negligible (solubility).
O.S.	. .	original solution.
ppt(d)	. .	precipitate(d).
sat(d)	. .	saturate(d).
sl.	. .	slightly.
sol.	. .	soluble.
soln.	. .	solution.
v	. .	very.

APPENDIX B

COMMON REAGENTS

The following details may be useful to students. Instructors will
find full lists of inorganic reagents in the works of Vogel and of Tread-
well-Hall (see p. 293). No exhaustive list of organic reagents is
available, but details of many of these reagents are given in the books
of Campbell, Cole and Plimmer, referred to on pp. 308 and 436.

ACIDS AND BASES

Reagent	Density g. per ml.	Approximate Concentrations		
		g. per 100 ml.	Molar	Normal
Hydrochloric acid HCl (conc.)	1·19	45	12M	12N
" " (dil.)	1·03	7·3	2M	2N
Nitric acid HNO₃ (conc.)	1·42	100	16M	16N
" " (dil.)	1·07	12·6	2M	2N
Sulphuric acid H₂SO₄ (conc.)	1·84	180	18M	36N
" " (dil.)	1·06	9·8	1M	2N
Acetic acid CH₃COOH (glacial)	1·05	105	17M	17N
" " (dil.)	1·01	12	2M	2N
Sodium hydroxide NaOH (dil.)	1·08	8·0	2M	2N
Ammonia NH₃ (conc.)	0·88	31	15M	15N
" " (dil.)	1·00	3·4	2M	2N

OTHER INORGANIC REAGENTS

Reagent (Aqueous Solution)		Approximate Concentrations	
		g. per 100 ml.	Molar
Ammonium carbonate	(NH₄)₂CO₃	20	2M
Ammonium chloride	NH₄Cl	21	4M
Barium nitrate	Ba(NO₃)₂	6·5	0·25M
Calcium chloride	CaCl₂	2·8	0·25M
Calcium hydroxide (lime water)	Ca(OH)₂	0·18*	0·02M*
Chlorine water	Cl₂	0 7*	0 1M*
Ferric chloride	FeCl₃	4·0	0·25M
Hydrogen sulphide water	H₂S	0·4*	0 025M*
Potassium iodide	KI	1·7	0·1M
Silver nitrate	AgNO₃	1·7	0·1M
Sodium carbonate	Na₂CO₃	10·6	1M
Sodium phosphate	Na₂HPO₄	2·8	0·2M

* Saturated solution.

ORGANIC SOLVENTS

Name	Formula	Boiling-Point	Density (g. per ml.)	Solubility of solvent in water (g. per 100 ml.)	Solubility of water in solvent (g. per 100 ml.)
Acetic acid .	$CH_3.COOH$	118°	1·05	∞	∞
Acetone .	$CH_3.CO.CH_3$	57°	0·79	∞	∞
Benzene .	C_6H_6	80°	0·89	0·08	0·2
Chloroform .	$CHCl_3$	61°	1·50	1	0·15
Ether .	$C_2H_5.O.C_2H_5$	35°	0·71	7	1·4
Ethyl acetate .	$CH_3.COOC_2H_5$	77°	0·90	9	3
Ethyl alcohol .	$C_2H_5.OH$	78°	0·79	∞	∞
Methyl alcohol .	$CH_3.OH$	65°	0·79	∞	∞
Petroleum ether .		40–60°*		0·05	0·1
" "		60–80°*	about 0·65	or less	or less
" "		80–100°*			
Toluene . .	$C_6H_5.CH_3$	111°	0·87	0·05	

* Mixtures of paraffin hydrocarbons boiling over these ranges.

APPENDIX C

APPROXIMATE MEASUREMENT OF SOLIDS AND LIQUIDS

In all qualitative work it is necessary to have a very rough idea of the quantities of solids and liquids used.

SOLIDS

In some preparations sample quantities of solids will be weighed by a demonstrator, and the student should compare his own quantities with these by eye. If such samples are not provided, a rough balance must be used. Solids vary so much in apparent density that it is impossible to give any rough standards of weight. Quantities of solids are often described in this book in terms of an arbitrary unit called a "spatula-point," which is a heap of the dimensions shown below.
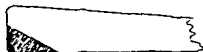
Plan   Side-view

Spatula-Point

Liquids

The student should know the appearance of the following volumes of liquids:

in an ignition-tube ($3'' \times \frac{1}{4}''$), 1 ml.

in a test-tube ($6'' \times \frac{5}{8}''$), 1 ml., 2 ml., 5 ml., 10 ml.

in a boiling-tube ($6'' \times 1''$), 2 ml., 5 ml., 10 ml., 20 ml.

When he is told to take these volumes in qualitative tests he can then judge them by eye, saving time.

Dropping-pipettes delivering drops of approximately 0·05 ml. are suitable for volumes up to 1 ml. Some liquids may be provided in bottles fitted with 1·0 or 2·0 ml. pipettes for approximate measurement. Others may be provided in automatic pipettes, which can be adjusted to deliver approximately 5, 10, 15, 20 or 25 ml.

The pipette consists of a boiling-tube in which an air-hole H has been blown, and is operated as follows. The reservoir, a bottle of 1-2 l. capacity with a tubulure in the side near the base, is raised so that liquid flows through the tube A until the pipette is filled above the mark. The reservoir is then lowered and the excess liquid over the mark runs back into it. The desired volume of liquid may now be run out of the tap T.

Where somewhat greater accuracy than may be obtained with the above methods is required, liquids may be measured with measuring cylinders (Fig. 5, 10; p. 64) or graduated pipettes (Fig. 5, 6, C; p. 59).
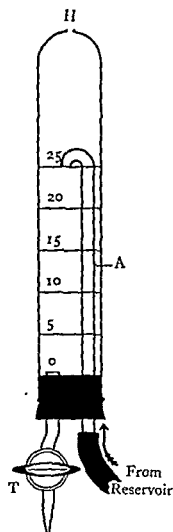
Automatic Pipette

Appendix D

ATOMIC WEIGHTS

Element	Symbol	Atomic Weight
Aluminium	Al	26·97
Antimony	Sb	121·8
Arsenic	As	74·91
Barium	Ba	137·4
Bismuth	Bi	209·0
Boron	B	10·82
Bromine	Br	79·92
Cadmium	Cd	112·4
Calcium	Ca	40·08
Carbon	C	12·01
Chlorine	Cl	35·46
Chromium	Cr	52·01
Cobalt	Co	58·94
Copper	Cu	63·57
Fluorine	F	19·00
Hydrogen	H	1·008
Iodine	I	126·9
Iron	Fe	55·85
Lead	Pb	207·2
Magnesium	Mg	24·32
Manganese	Mn	54·93
Mercury	Hg	200·6
Nickel	Ni	58·69
Nitrogen	N	14·01
Oxygen	O	16·00
Phosphorus	P	30·98
Potassium	K	39·10
Silicon	Si	28·06
Silver	Ag	107·9
Sodium	Na	23·00
Strontium	Sr	87·63
Sulphur	S	32·06
Tin	Sn	118·7
Zinc	Zn	65·38

Appendix E

LOGARITHMS

	0	1	2	3	4	5	6	7	8	9	1 2 3	4 5 6	7 8 9
10	0000	0043	0086	0128	0170	0212	0253	0294	0334	0374	5 9 13 4 8 12	17 21 26 16 20 24	30 34 38 28 32 36
11	0414	0453	0492	0531	0569	0607	0645	0682	0719	0755	4 8 12 4 7 11	16 20 23 15 18 22	27 31 35 26 29 33
12	0792	0828	0864	0899	0934	0969	1004	1038	1072	1106	3 7 11 3 7 10	14 18 21 14 17 20	25 28 32 24 27 31
13	1139	1173	1206	1239	1271	1303	1335	1367	1399	1430	3 6 10 3 7 10	13 16 19 13 16 19	23 26 29 22 25 29
14	1461	1492	1523	1553	1584						3 6 9 3 6 9	12 15 19 11 14 17	22 25 28 20 23 26
18	2553	2577	2601	2625	2648	2672	2695	2718	2742	2765	2 5 7 2 4 7	9 12 14 9 11 14	17 19 21 16 18 21
19													
20													
21													
22													
23													
24													
25	3979	3997	4014	4031	4048	4065	4082	4099	4116	4133	2 3 5	7 8 10	11 13 15
26	4150	4166	4183	4200	4216	4232	4249	4265	4281	4298	2 3 5	6 8 9	11 13 14
27													
28											2 3 5	6 8 9	11 12 14
29											1 3 4	6 7 9	10 12 13
30	4771	4786	4800	4814	4829	4843	4857	4871	4886	4900	1 3 4	6 7 9	10 11 13
31	4914	4928	4942	4955	4969	4983	4997	5011	5024	5038	1 3 4	6 7 8	10 11 12
32	5051	5065	5079	5092	5105	5119	5132	5145	5159	5172	1 3 4	5 7 8	9 11 12
33	5185	5198	5211	5224	5237	5250	5263	5276	5289	5302	1 3 4	5 6 8	9 10 12
34	5315	5328	5340	5353	5366	5378	5391	5403	5416	5428	1 3 4	5 6 8	9 10 11
35	5441	5453	5465	5478	5490	5502	5514	5527	5539	5551	1 2 4	5 6 7	9 10 11
36												4 5 6	7 8 10 11
37												3 5 6	7 8 9 10
38												3 5 6	7 8 9 10
39												3 5 6	7 8 9 10
40												3 4 5 6	8 9 10
41												3 4 5 6	7 8 9
42												3 4 5 6	7 8 9
43												3 4 5 6	7 8 9
44												3 4 5 6	7 8 9
45												3 4 5 6	7 7 9
46												3 4 5 5	7 7 8
47												3 4 4 5	6 7 8
48												3 4 4 5	6 7 8

LOGARITHMS

	0	1	2	3	4	5	6	7	8	9	1 2 3	4 5 6	7 8 9
50													
55													
60													
65													
70													
75	8751	8756	8762	8768	8774	8779	8785	8791	8797	8802	1 1 2	2 3 3	4 5 5
76													
77													
78													
79													
80	9031	9036	9042	9047	9053	9058	9063	9069	9074	9079	1 1 2	2 3 3	4 4 5
81	9085	9090	9096	9101	9106	9112	9117	9122	9128	9133	1 1 2	2 3 3	4 4 5
82	9138	9143	9149	9154	9159	9165	9170	9175	9180	9186	1 1 2	2 3 3	4 4 5
83	9191	9196	9201	9206	9212	9217	9222	9227	9232	9238	1 1 2	2 3 3	4 4 5
84	9243	9248	9253	9258	9263	9269	9274	9279	9284	9289	1 1 2	2 3 3	4 4 5
85	9294	9299	9304	9309	9315	9320	9325	9330	9335	9340	1 1 2	2 3 3	4 4 5
86	9345	9350	9355	9360	9365	9370	9375	9380	9385	9390	1 1 2	2 3 3	4 4 5
87													
88													
89													
90	9542	9547	9552	9557	9562	9566	9571	9576	9581	9586	0 1 1	2 2 3	3 4 4
91	9590	9595	9600	9605	9609	9614	9619	9624	9628	9633	0 1 1	2 2 3	3 4 4
92	9638	9643	9647	9652	9657	9661	9666	9671	9675	9680	0 1 1	2 2 3	3 4 4
93	9685	9689	9694	9699	9703	9708	9713	9717	9722	9727	0 1 1	2 2 3	3 4 4
94	9731	9736	9741	9745	9750	9754	9759	9763	9768	9773	0 1 1	2 2 3	3 4 4
95	9777	9782	9786										
96													
97													
98													
99													

INDEX

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Italic type denotes a principal reference.

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